Silsesquioxanes : alternative approaches and methods of synthesis.

Thesis

Silsesquioxanes: Alternative approaches and methods of synthesis

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STATEMENT

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ABBREVIATIONS

In the following table are listed the most frequently used abbreviations throughout this thesis.

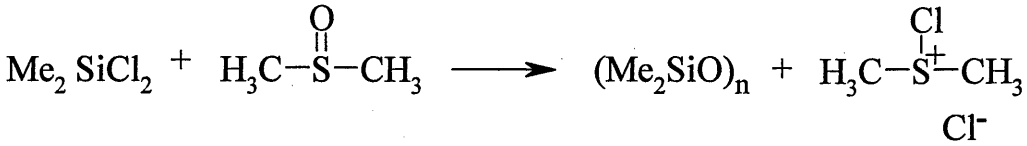
Ph	Phenyl group
Br	Broad
Cp	Cyclopentyl
Cy	Cyclohexyl
d	Doublet
DCC	Dicyclohexylcarbodiimide
DMSO	Dimethylsulfoxide
EI	Electron Ionisation
FAB	Fast Atom Bombardment
FT-IR	Fourier Transform Infra red
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HPLC	High Performance Liquid Chromatography
Hz	Hertz
MS	Mass Spectrometry
m	Multiplet
MALDI-TOF	Matrix-Assisted Laser Desorption Ionisation Time of Flight
MIBK	Methyl *iso*-butyl ketone
NMR	Nuclear magnetic resonance
ppm	Parts Per Million
q	Quartet
s	Singlet
t	Triplet

TBAF	Tetra-*n*-butylammonium fluoride
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Tretramethylsilane
TMS-Cl	Trimethylchlorosilane

ABSTRACT

The synthesis of silsesquioxanes from chlorosilanes has been investigated in this thesis using the "non aqueous" hydrolysis approach.

DMSO (dimethylsulfoxide) has been used as a source of oxygen for the "non aqueous" hydrolysis involving di- and trichlorosilanes. With dichlorosilanes the reaction led to D rings and in particular to a D3 ring according to the following scheme:



Under the conditions of the reaction, D3 is converted into larger and more stable rings such as D4 and D5.

Other oxygen donor compounds have been studied and, as for DMSO, the result was the formation of D3 which was subsequently converted into larger rings.

The mechanism has also been investigated and we found that D ring formation occurs via the formation of α,ω-dichlorosiloxanes which are converted to D rings via an intramolecular cyclisation.

DMSO has also been used to react with trichlorosilanes leading to cages. As for the conventional hydrolysis we expected the formation of T8 cages but to our surprise we obtained T6. Several trichlorosilanes are commercially available and so we performed the "non aqueous" hydrolysis using trichlorosilanes with a range of substituents. This provided a route to different T6s from the trichlorosilane which have previously been unobtainable.

We also synthesised trichloroilanes via hydrosilylation in order to obtain trichlorosilanes carrying other functionalities which could be used to synthesise a new set of T6s which again could not be prepared by ordinary hydrolysis.

We performed the "non aqueous" hydrolysis of trichlorosilanes using the other oxygen donor compounds but the results were not as satisfactory as with DMSO.

Our last aim was the synthesis of cages (in particular T8 cages) carrying different arms on the silicon atoms. The synthesis of cyclic cis-polyols was the first step to achieve this aim. We used a range of approaches to the synthesis of the polyols but the most satisfactory was Shchegolikhina's method. With this method we were able to isolate a number of new product such as the cis cyclopentyltriol and the cis cyclohexyltetrol.

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CHAPTER 1

INTRODUCTION

1.1- Silicon and its chemistry.

Silicon is found in nature bound to oxygen as silica and silicates and it is present in the earth's crust at a level of about 28%[1], second in elemental abundance only to oxygen (49.5%)[2, 34, 36].

Silicon belongs to the fourth group of the Periodic Table and thus its chemistry is often compared with that of carbon despite the fact that it does not possess the multitude of stable bonding configurations of carbon. The enhanced reactivity of silanes when compared to the analogous carbon compounds, particularly to nucleophilic substitution, is generally related to three characteristics of silicon: its larger size, lower electronegativity and the availability of low energy d orbitals.

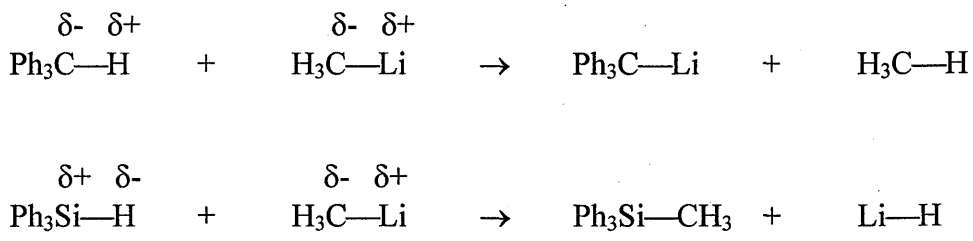
The position of silicon towards the top of the Periodic Table means that it is a semi-metal. In fact it possesses few of the metallic features of the heavier elements of its group with only a slight tendency to form stable divalent compounds. Silicon forms bonds with most of the other elements of the Periodic Table. As result, it has an important inorganic, organic and polymer chemistry.

The greater electropositivity of the silicon atom, compared with that of the carbon atom, means that whilst both silicon-chlorine and carbon-chlorine bonds are polarised in the sense:

Figure 1.1

the density of the positive charge, δ^+, is greater on the silicon atom than on the carbon. This contributes to silicon being more readily attacked by nucleophilic reagents such as OH^-.

Silicon is sometimes polarised in the opposite sense to carbon, in that the positive charge is more likely to be localised on the silicon atom when compared with similar carbon compounds. This difference is exemplified by the two reactions shown in the following Scheme[3]:



Scheme 1.1 – Difference in reactivity according to the polarisation.

This behaviour is compatible with the higher rate of bimolecular nucleophilic substitution which typifies the second period of elements, and ensures that substitution at silicon takes place with much poorer leaving groups than substitution at carbon. Thus the Si—F, Si—OR, Si—C and Si—H bonds are all cleaved by appropriate nucleophiles.

This susceptibility to nucleophilic attack means that the halosilanes, and particularly chlorosilanes, are good starting materials for the formation of many compounds, especially for Si—O bond formation. This is also, in part, due to the strength of the bond silicon forms with electronegative elements, particularly oxygen. A comparison of Si—X and C—X bond strengths (Table 1.1) clearly shows the way in which the two elements are different. The bonds between silicon and halogens or oxygen are exceptionally strong (Si—F is one of the strongest single bonds between two elements).

Bond	Compound	D/ kJ mol^{-1}	r/nm	Bond	*D*/ kJ mol^{-1}	r/nm
Si–C	Me_4Si	318	0.181	C–C	334	0.153
Si–H	Me_3SiH	339	0.148	C–H	420	0.109
	Cl_3SiH	378, 382				
Si–O	Me_3SiOMe	531	0.163	C–O	340	0.141
	$(Me_3Si)_2O$	812				
Si–N	$(Me_3Si)_2NH$	320	1.174	C–N	335	0.147
Si–Cl	Me_3SiCl	471	0.205	C–Cl	335	0.178

Table 1.1 – Comparison of the approximate bond dissociation energy (D) and bond length (r) for Si—X and C—X compounds.

In contrast with the strengths of the bonds between silicon and the most electronegative elements, the bonds between silicon and nitrogen or silicon and hydrogen are much weaker if compared with similar carbon compounds. This, as we will see, has important consequences in the relative reactivity of silanes with respect to hydrocarbons.

It has been suggested that stronger bonds are formed with more electronegative groups because of the increase in contribution from an ionic structure of the type $Si^{\delta+}$—$X^{\delta-}$. Table 1.2[4] shows a comparison of the ionic character of the bonds involving silicon and carbon with other atoms in polydimethylsiloxanes.

Element X	Calculated ionic character (%)	
	Si—X	C—X
Si	—	12
C	12	—
H	2	4
O	50	22

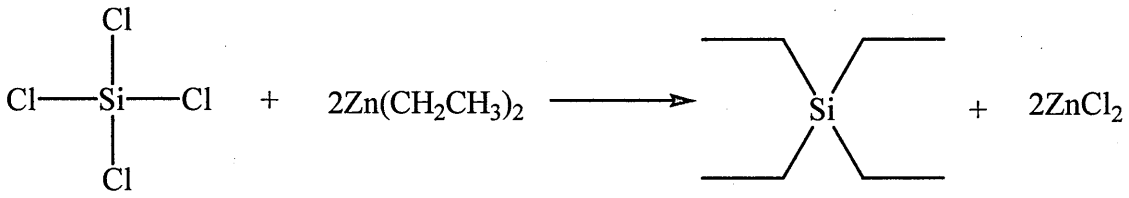
Table 1.2 – Comparison of the ionic character of the bonds between silicon and carbon with elements with different electronegativity.

The values in the table clearly show a high ionic character of the bond between silicon and oxygen in comparison with the bond between carbon and oxygen: this separation of charge explains the higher susceptibility of the silicon to nucleophilic attack.

Such a view can similarly explain the large bond angle and the low bending force constants for Si—O—Si.

1.2 – Organosilicon chemistry.

The study of organosilicon chemistry is over a 100 years old. Organosilanes are not natural compounds[2a] therefore they need to be synthesised in the laboratory and the first preparation was conducted by Friedel and Crafts who reacted silicon tetrachloride with diethylzinc to form tetraethylsilane, the first organosilane[2d].



Equation 1.1 - Friedel and Crafts's scheme of reaction.

This was developed much further by Stanley Kipping[44], who in 1937 synthesised a range of organosilicon compounds by reaction of $SiCl_4$ with several different Grignard reagents. Kipping also discovered that, when triethylchlorosilane is reacted with water it gives an unstable compound identified as the corresponding silanol which combines with itself to give hexaethylsiloxane. He characterized his products as "glue like" and unimportant. He did not recognise the importance of such reactions and in fact, at the end of his career, he said to a conference: *"We have considered all the known types of organic derivatives of silicon . . . the prospect of any immediate and important advance in this section of chemistry does not seem very hopeful".*

The first chlorosilane synthesised commercially was dimethyldichlorosilane by Eugene Rochow[2] and Richard Müller in 1941-1942[2] using the direct reaction of silicon and chloromethane:

$$Si + 2MeCl \rightarrow Me_2SiCl_2$$

Equation 1.2 – Method of synthesis of commercial chlorosilane.

With the advent of this process, functional organosilanes became widely available for the first time, although the variety of available alkylsilanes was initially somewhat limited.

Nowadays silane monomers are turned into silicon based polymers, silicones, which are high value products in the developed world: over 10^9 kg of silicones are produced each year.

The monomers, from which polymeric organosilanes are made, also possess unusual properties and thus small organosilanes are increasingly utilised in a variety of different industrial applications. In the pharmaceutical industry, for instance, silane protecting groups are used for organic functional groups both because of their easy introduction and cleavage and because of the relatively low toxicity of the silane species and their by-products.

The increased volatility of organosilicon-functionalised compounds, when compared with the analogous hydrogen functionalised species, has been exploited by mass spectrometrists to improve sample introduction and by those interested in fabricating semiconductors using the chemical vapour deposition (CVD) process[11]. The use of organosilanes to control carbon-carbon bond formation in organic synthesis is increasingly exploited and remains an active area of research.

1.3- Preparation of chlorosilanes: the "Direct Process"[170].

As described earlier, chlorosilanes had been known since 1904 when they were first prepared from silicon tetrachloride and Grignard reagents. However methylchlorosilanes could not be conveniently prepared using this method. In the 1940s Eugene Rochow[2] at the General Electric Company developed a method to synthesise methylchlorosilanes. The Rochow method, usually called the "Direct Process"[162-164,166], involves direct synthesis of chlorosilanes[165] from alkyl and aryl chlorides in the presence of a catalyst[169] according to the general reaction:

$$2RCl + Si \longrightarrow R_2SiCl_2 + heat$$

Equation 1.3 – Reaction scheme of the "Direct Process".

The process is most efficient when R=CH_3 (the reaction scheme is shown in Equation 1.2). Chloromethane gives, in addition to Me_2SiCl_2, small amount of the trichloro- and monochloro- silanes[167]. Me_4Si, $MeHSiCl_2$, $SiCl_4$, H_2, CH_4, C_2H_6, $Me_xSi_2Cl_{6-x}$ and $Me_x(SiCH_2Si)Cl_{6-x}$ are also present as by-products.

$$2CH_3Cl + Si \xrightleftharpoons[250\text{-}300\,^0C]{Cu} (CH_3)_2SiCl_2$$

Equation 1.4 – "Direct Process" using chloromethane.

With chloromethane the process is commonly run in the temperature range 250-350 °C and at 1-5 atm pressure. On an industrial scale, ground silicon is reacted with gaseous chloromethane in a fluid bed reactor. Besides silicon, small amounts of other elements must be introduced into the reaction mixture to achieve a reactive contact mass. Metallographic analysis has shown that the catalytically active portion of the solid, where the silicon is consumed, contains certain of these elements alloyed into the silicon surface. The catalytic elements, usually metals or metalloids, are introduced by mixing, grinding, sintering, or melting with silicon.

Copper is the best catalyst for use with chloromethane because of a fortuitous combination of properties such as: (1) the ready reduction of copper salt by silicon[168]; (2) the oxidation of copper metal by MeCl to form CuCl and possibly transient gaseous CuMe species; (3) the fast diffusion of copper through solid silicon; (4) other properties related to the solid state physics of copper-silicon alloys.

This method is now used commercially to produce methylchlorosilanes on a large scale[171].

One of the most important reactions of methylchlorosilanes is their hydrolysis. This reaction is used by industry because of the low cost of the reagents (water) and because the HCl generated can be recycled to form chloromethane from methanol.

1.4 –Silicones: general properties and applications.

The commercial availability of organosilanes has been a result of the fact that the silicones $(RR'SiO)_n$ derived from them are widely used in different industries for a broad variety of applications. Much of the impetus for the development of organosilicon chemistry in general has arisen from the utility of silicon polymers and the necessity to optimise their preparation and properties[141,142]. Although silicones are expensive, they have had remarkable commercial success: several billion kilograms of silicones are currently produced per year[46]. The popularity of silicones is due to their properties[47], which cannot be matched by organic replacements and the fact that only small amounts of materials are frequently required to achieve the desired results.

We shall start this section with a brief description of the properties and the uses of silicones and some representative applications.

Silicones, in the absence of an acidic or basic catalyst, are exceptionally thermally stable. Degradation of dimethylsilicone fluids begins at 350°C and phenylsilicones are stable to higher temperatures. This thermal stability can be exploited in seals for kitchen appliances and hair dryers etc.

The relative permittivity (dielectric constant) of silicone fluids is very low for low-molecular weight oligomers[143-145] and about 2.75 for higher-molecular weight materials (by comparison the permittivity of acetone and of water is 20.7 and 78.5 respectively[45]). These values are not dramatically affected by the temperature. Under

conditions of extreme temperature, when decomposition of the silicone occurs, the oxidative decomposition product is silica, another excellent insulator. Thus silicones are widely used in wire coatings, motor insulators and transformers etc.

Dimethylsilicones are known to be exceptionally hydrophobic[146]. This results from two phenomena: firstly the methyl group provides hydrophobic characteristics to the polymer and secondly the flexibility of the silicon polymer chain permits the rearrangement of the polymer backbone such that the methyl groups may orient themselves at an interface. The chain flexibility arises from the very large angle of the Si-O-Si linkage (ca. 145°)[147].

The resistance to liquid water has made silicone materials (both fluid and cross linked polymers) the compounds of choice for moisture barriers, including fabrics, hard surface (waxes for automobiles), architectural materials (sealants for windows) and potting materials (to protect circuits boards from liquid water) etc.

Organofunctional siloxanes are a broad class of polymers in which the conventional polysiloxanes are modified by incorporating a variety of chemically reactive groups along the siloxane chain. New materials with a wide spectrum of properties can be designed[148-153]. The properties of organofunctional siloxanes can be tailored to be similar to those of the parent polydimethylsiloxanes, or entirely new characteristics can be introduced.

Organofunctional siloxanes are used in many commercial applications nowadays and many more are emerging as reliable sources became available. Some of the most common examples are the aminofunctional siloxanes which are widely used in textiles and household care products. Epoxy- and acrylic-functionalised siloxanes have application in UV curable coatings, paints and resin modification, and glycol-

functionalised polysiloxanes are well-known surfactants used in foam production and personal care applications.

There follows a more detailed description of the more common applications of organofunctional siloxanes.

Cosmetic applications. Silicones have been used in personal care products for over 30 years and are present in many well-known hair and skin care preparations [5,6,7]. The use of silicones in hair care applications has been limited because of the difficulty in controlling the deposition of nonfuctional polydimethylsiloxane. However, siloxanes modified with amine or polyether substituents have been developed which provide substantive, durable conditioning properties typically at addition levels of 1-5% in shampoo formulations. Improved depth and colour retention can be achieved in hair dying by pre-treating the hair with organofunctional siloxane formulations containing amino, amido or quaternary ammonium group[8]. The conditioning properties imparted by polyether functional siloxanes tend to be lost after two or three weeks whereas the aminofunctional analogues still show the effect of improved combing and higher gloss after six weeks.

A recent development in skin care technology has been the use of silicones in suntan lotion[9]. Nonfunctional polydimethylsiloxanes are currently used in lotions together with UV-B protecting agents. These absorb the harmful UV wavelengths while allowing the tanning UV-A wavelengths to pass through. Attempts have been made to prepare a single polymer in which the lubrication and soft-feel of the silicone can be coupled with a UV absorbing species. This has been achieved by grafting up to 20 mol % of a chromophore, based on *p*-aminobenzoic acid or *p*-methoxycinnamic acid, onto the silicone backbone.[9,10,11] These polymers must be hydrolytically stable, very pure and have relatively low viscosity to be compatible with cosmetic preparations.

Textiles. Organofunctional siloxanes, particularly the aminosiloxanes, have been used as fabric treatments by textile processors for many years[13,14]. This is well documented in several recent reviews[15,16].

A polymer containing less than 0.4 mol % diaminopropyl alkoxy endgroups can be made substantive to wool and prevent shrinkage in an automatic wash cycle. Treatment of polyester fibres with a polymer containing similar pendant groups changes the fibre's physical characteristics giving bounce, resilience and enhanced air entrapment. Aminofunctional siloxanes also give improved durable press appearance without the need for conventional cross-linking resin[17].

Plastics and resins modification. Organofunctional siloxanes have been used extensively to modify most classes of organic resins. For example, aminofunctional polysiloxanes have been used as additives to modify the surface characteristics of urethanes, epoxides and acrylates[18,19]. The relationship between microstructure, morphology and surface properties in polycarbonate-siloxanes copolymers has been studied and solvent effects in solution cast films, elucidated[20,21]. Siloxane-polyimide copolymers have been described to import improved resistance to moisture and processability for high temperature engineering resins[22,23,24]. Polysulfones are another important class of high performance thermoplastics which have been modified with siloxanes by reacting the phenol-terminated polysulfone with dialkylamine terminated siloxanes to give block copolymers.

A new class of hydrophilic silicone pressure sensitive adhesives (PSAs) has been formulated using siloxane polyether graft copolymers. Some of the most frequently used silicones are α,ω-difunctional polydimethylsiloxanes which can be used either as additives to both thermoplastic and thermoset resins or as co-monomers in the formation of siloxane-organic block copolymers.

There are many other fields where silicones have found applications, one of them is as liquid-crystal polymers (LCPs) used because of their unique electrical, optical and thermal properties[25-28].

1.5 – The nature of the Si-O-Si bond.

When Linus Pauling developed his first theories of chemical bonding, based on quantum mechanics, silica and its related organic and inorganic compounds played a marginal role in its justification. Silicones, in particular, were not known in the thirties.

In organometallic chemistry, back donation generally occurs from the lone pair on an adjacent heteroatom into an appropriately orientated *d* orbital on a metal centre[29].

Early work, before the 1960s, assumed that the *d* orbitals on silicon could participate in such back donation[37], as supported by NMR spectroscopy[37,38]. More recent work based on *ab initio* calculations, NMR spectroscopy[39] and other experiments[40], suggests that the significant participation of d orbitals is precluded due to the high energy of such orbitals. Other orbitals, therefore, must be involved in the formation of these types of bond[41, 42].

Studies have suggested that, as silicon has low lying σ* orbitals with the correct symmetry, and because of silicon's low electronegativity, these orbitals can participate in a π-type back-bonding interaction[43].

Several observations can be explained taking into account such back donation. In silanols, for instance, the hydrogen on the OH group is more acidic compared with the same hydrogen in alcohols. Back donation between the lone pair on the adjacent heteroatom with either the d orbitals or σ* orbitals of the silicon lead to the doubly

bonded species **1.1**. Figure 1.2 shows how this back donation occurs involving either d orbitals or σ* orbitals.

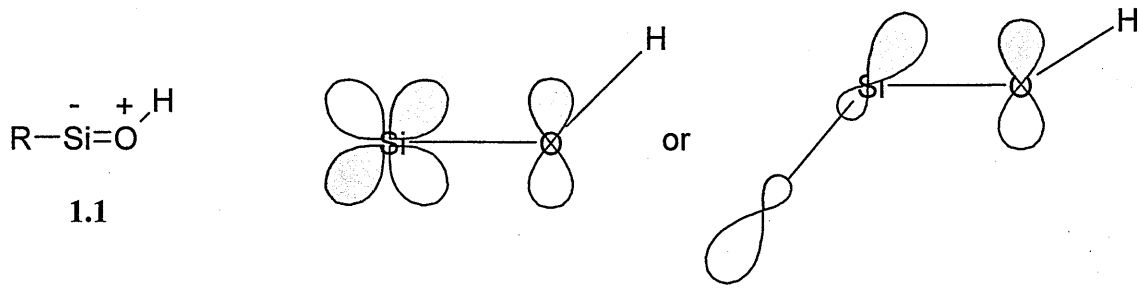


Figure 1.2 – Scheme of back donation.

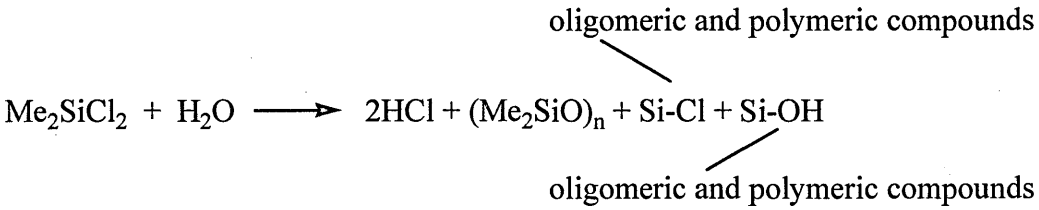
Back donation can also explain the extremely low bending force constant around Si—O—Si bonds. Usually bond lengths and bond angles involving silicon are affected not only by steric crowding, but also by the nature of the central atom. In bonds such as Si—C—Si the tetrahedral central carbon can be deformed in the presence of bulky groups. When the central atom is a heteroatom such as oxygen, the angles are deformed even in the absence of a bulky group. Again, back donation explains this behaviour; the back donation of the lone pair on the oxygen atom results in a changing of the hybridisation from sp^3 (tetrahedral) to sp (linear)[194]. $Ph_3SiOSiPh_3$ is an extreme case of this where the Si—O—Si bond angle is 180° [194].

1.6 - Hydrolysis of chlorosilanes: Synthesis of silicones.

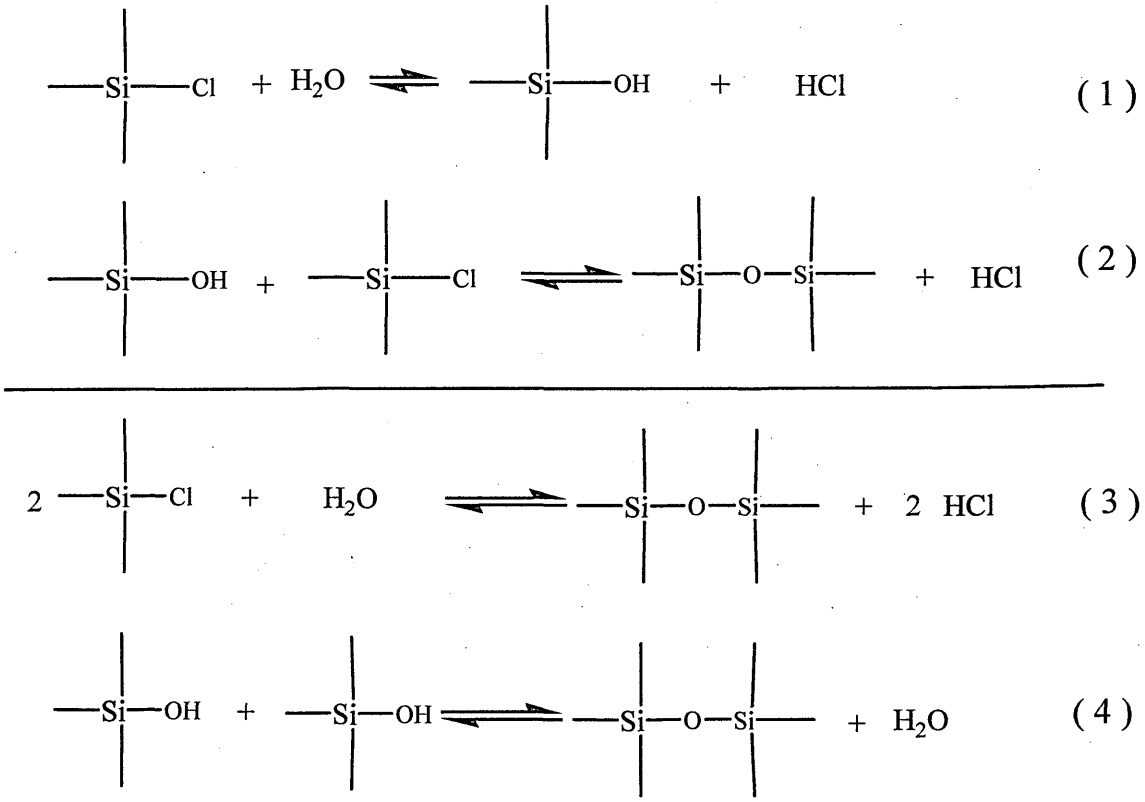
1.6.1 - Hydrolysis with excess water.

The oxygen silicon bond is stronger than those of all other elements to silicon except fluorine, and so many compounds containing an Si-X bond can be hydrolysed, which provides a route to silicon oxygen derivatives. The basic starting materials for silicones are the dialkyldichlorosilanes (usually dichlorodimethylsilane). The

mechanism for hydrolysis in the presence of excess water involves the hydrolysis of the starting material to a silanediol, which then condenses to give disiloxanes etc., as shown in Scheme 1.3. Because of the strong silicon-oxygen bond formed during hydrolysis, this is a highly exothermic process[155, 156]. More commonly, incomplete hydrolysis of chlorosilanes leads to silanols, containing an Si—OH group, and siloxanes, possessing the Si—O—Si linkage. Thus, hydrolysis of dimethyldichlorosilane often produces a mixture of cyclic siloxanes and chlorine- and/or hydroxyl- end-blocked linear polysiloxanes according to the formulation:



The chemical bond transformations are shown in Scheme 1.2:



Scheme 1.2

Equation (3) is the sum of equations (1) and (2) and represents an equilibrium, controlling the degree of hydrolysis. Thus, the ratio of HCl to H_2O determines the overall ratio of Si—Cl to Si—O—Si[157]. In fact, the heat of reaction for this reaction is endothermic, when a stoichiometric amount of water is used, but is exothermic when excess water is used. This is due to the heat of vaporisation of hydrogen chloride. Industrially, anhydrous HCl can be recovered from the hydrolysis of chlorosilanes by using saturated 42% aqueous HCl as the source of water.

The HCl from hydrolysis can also lead to unwanted cleavage of organic groups attached to the silicon. The rate of cleavage of Si—R increases in the order R = Me < CH_2=CH_2 < Ph < H and the cleavage of R—Si increases as the number of such organic groups on the silicon increases. The cleavage of methyl groups attached to silicon is usually not encountered in commercial hydrolysis and this explains the importance of methylchlorosilanes within the industry. The cleavage reaction of other substituents can be suppressed by keeping the hydrolysing acid dilute and by using a low temperature.

The hydrolysis represented in Equation 3 in scheme 1.3 is rapid, being limited by the rate of transfer of reactants and products across the siloxane/acid phase boundary. For this reason, hydrolysis reactions are normally performed in a continuously fed hydrolysis "loop", where recirculation pumps impart a high turbulence to the reacting mixture[191]. The phase separation of the products from the acid must be followed by one or more aqueous washes to drive reaction 3 to completion. To ease the separation of phases a water immiscible, siloxane compatible, solvent is added to increase the density difference between the upper and lower liquid layers.

Both cyclic and linear siloxanes are produced by the hydrolysis of difunctional silanes. The relative proportion of oligomers depends upon the substituents and conditions employed. The hydrolysis of dimethyldichlorosilane frequently gives a weight ratio of cyclic to linear siloxanes of about 1:1. Octamethylcyclotetrasiloxane (D_4)[140], shown in Figure 1.3, normally makes up at least 80% of the cyclic fraction. The formation of linear dimethylsiloxane can be suppressed by the use of organic co-solvents (particularly diethyl ether)[192].

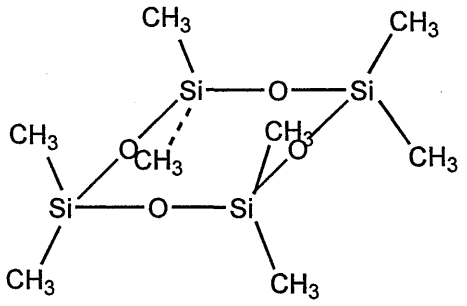


Figure 1.3

An increased ratio of cyclic to linear siloxanes is also obtained by the vapour hydrolysis of dimethyldichlorosilane at 1 atm pressure with solvent vapour dilution at temperatures of over 200 °C.

The hydrolysis of trichlorosilanes leads to a complex mixture of three dimensional siloxanes including cages and resins. The reaction rate, the degree of oligomerization and the yield of the polyhedral compounds formed, depend upon numerous factors such as:

1 – the concentration of the initial monomers in solution;

2 – the nature of the solvent;

3 – the character of the substituent R in the initial monomers $RSiY_3$;

4 – the nature of leaving group Y in the initial monomers $RSiY_3$;

5 – the type of catalyst;

6 – the temperature;

7 – the amount of water;

8 – the solubility of the polyhedral oligomers formed.

Whilst all these factors have been studied, little is known of the detailed mechanism of three dimensional siloxane formation. Although no industrial methods have been reported in the literature, hydrolytic polycondensation is the most universal synthetic route to oligosilsesquioxanes and their homoderivatives.

The synthesis of the most important oligomers has been carried out in an organic solvent using water in the presence of an appropriate acid or base catalyst. As expected, high concentrations of the reagents facilitates the formation of complex three dimensional polymers. When dilute solutions are used, intramolecular cyclizations predominate, leading to polyhedral oligomers.

Polyhedral silsesquioxanes are formed in both polar and non-polar solvents, but non-polar solvents such as cyclohexane or benzene, usually favour the formation of oligosilsesquioxanes from $HSiCl_3$. The rate of hydrolytic polycondensation of alkyltrichlorosilanes depends on the length and branching of the alkyl group on the silicon atom. Usually the yield of caged formed in aqueous hydrolysis is high for the methyl substituent and decreases with the length of the chain and with the extent of branching.

As mentioned earlier, the formation of polyhedral silsesquioxanes from linear, cyclic and polycyclic monomers by the hydrolytic polycondensation of trifunctional monomers, $XSiY_3$, occurs only in the presence of either an acid or a base catalyst. For example, HCl, $ZnCl_2$, $AlCl_3$, $HClO_4$ and CH_3COOH have all been used as catalysts for the preparation of octaalkylsilsesquioxanes.

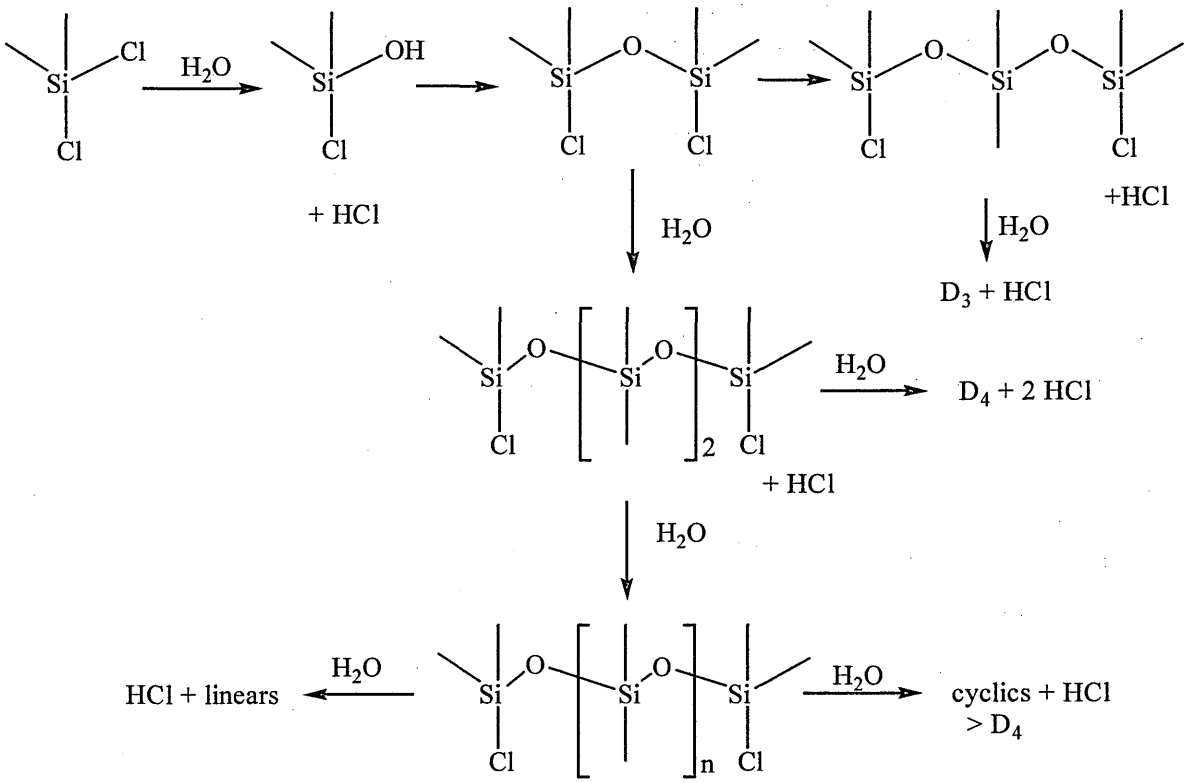
The first step of oligosilsesquioxane formation is usually carried out at low temperatures. Variations in the temperature may affect the solubility of the hydrolytic polycondensation products, thus facilitating the isolation of oligoorganosilsesquioxanes and their homo derivatives from the solution. The formation of oligoorganosilsesquioxanes from organotrichlorosilanes (Scheme 1.3) may occur without the addition of extra water if wet methanol or ethanol is used as the solvent.

$$RSiCl_3 \xrightarrow[H_2O]{MeOH} (RSiO_{1.5})_n$$

Scheme 1.3

1.6.2 – Scarce water hydrolysis: hydrolysis of alkoxysilanes.

The mechanism of silicone formation from dichlorosilanes, when the concentration of water is low, involves the hydrolysis of dichlorodimethylsilane to a chlorosilanol [158], as shown in Scheme 1.4. This subsequently dimerizes to give the 1,3-dichlorosiloxane which can dimerize or homologate to give the chlorine-terminated tetra- or trisiloxane which in turn cyclizes or leads to further linear polymers.



Scheme 1.4 – Mechanism of scarce water hydrolysis.

The predominant products are normally cyclics, and D_4 is predominant with respect to D_3 when water is used in this process[140,159]. The formation of linear siloxane can be reduced by using an organic solvent[139].

1.6.3 – Ring-chain equilibria.

In the synthesis of siloxane polymers, linear and cyclic siloxanes are present in an equilibrium mixture. The equilibrium mixture obtained from hydrolysis of R_2SiX_2 monomers is identical to that obtained by ring opening polymerisation of rings such as octamethylcyclotetrasiloxane, D_4. Such an equilibrium mixture contains about 13% D_4-D_{10} and 2-3% D_{10}-D_{400}, the remainder being the linear siloxane. D_3 has a ring strain energy of about 16-21kJ mol^{-1}, and is not present in equilibrium mixtures below 150 °C. The other cyclics have virtually no ring strain energy and D_4 is the most favoured ring. The molecular weight of the linear siloxanes is governed by a competition with species capable of forming endblocks at the chain ends. Such species can be eliminated by forming the equilibrium mixture from pure D_4 when the only end groups present are those introduced by the catalyst. If the catalyst is present in very low levels the molecular weight of the linear siloxane can be very high. Polymerisation of pure mixed dimethyl cyclics catalysed by a few hundred ppm of anhydrous KOH proceeds slowly (in a few hours at a temperature of 100-200 °C) to yield a gum polymer with a molecular weight up to several million. The end groups in the chains are Si-OH and Si-OK species.

At equilibrium in the dimethylsiloxane system, the concentration of each cyclic, other than D_3, and the ratio of total cyclics to total linear siloxane is practically independent of the temperature. Above 150 °C the vapour pressure of the smaller cyclic siloxanes becomes appreciable. If the pressure above an equilibrating mixture of liquid polydimethylsiloxanes at temperatures in the range of 150-250 °C is kept below the equilibrium vapour pressure of cyclics, a complete depolymerization of the linear siloxane occurs and a vapour mixture of D_3, D_4, D_5 and D_6 is formed. As the temperature is increased, from 300 to 600 °C the mole fraction of D_3 in the vapour

increases to a high level. Pure D_3 and D_4, suitable for the production of silicone gum, may be produced commercially by such processes based on depolymerization of polydimethylsiloxane oligomers with alkali metal hydroxides[193].

1.7 – Nomenclature.

1.7.1 – Silanes

As with carbon, silicon nomenclature is based on the simplest hydrosilane, silane itself (SiH_4). The exchange of H for other substituents leads to compounds that are named, as with organic compounds, with alphabetic order taking precedence:

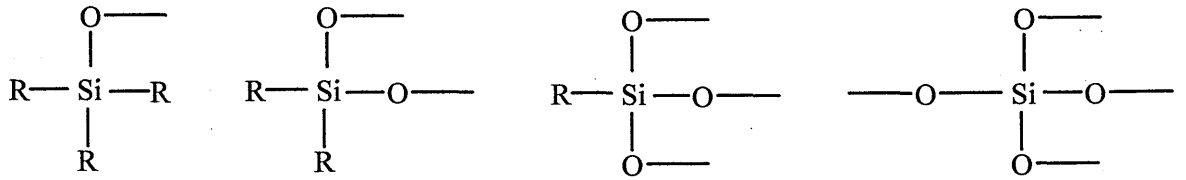
H_3SiSiH_3	disilane
Me_2SiCl_2	dichlorodimethylsilane (dimethyldichlorosilane)
$Ph_3SiSiMe_3$	1,1,1-trimethyl-2,2,2-triphenyldisilane

The majority of the compounds discussed in this thesis are silanes and, mostly, siloxanes, therefore it is useful to give a detailed summary of the nomenclature commonly used for such compounds.

1.7.2 – Siloxanes

The basic building blocks produced by the silicone industry contain a silicon oxygen bond and are known as siloxanes.

Silicon components are differentiated by the number of oxygen attachments: M = monofunctional, D = difunctional, T = trifunctional and Q = quadrifunctional as shown in Figure 1.4



M unit D unit T unit Q unit

Figure 1.4

Polysiloxanes are silicone polymers:

$H_3Si(OSiH_2)_nOSiH_3$ n = 0, disiloxane

n = 4, hexasiloxane

Cyclic silanes systems are numbered like the carbocyclic systems but named as *cyclo*polysilanes. Similarly, cyclic siloxanes are named according to the number of silicon atoms, appended functional groups and the addition of the prefix *cyclo*.

The permethylated cyclosiloxanes are commonly described using the General Electric nomenclature where cyclic siloxane names are based on the D unit followed by a number which indicates the number of D units in the ring.

Thus D_3 will be a cyclic siloxane formed by 3 siloxane D units as shown in Figure 1.5a. Cyclic siloxanes containing substituents other than methyl groups are named in the same way except that the nature of the group is indicated on the top left of the unit letter, therefore the molecule in Figure 1.5b would be $^{HPh}D_4$.

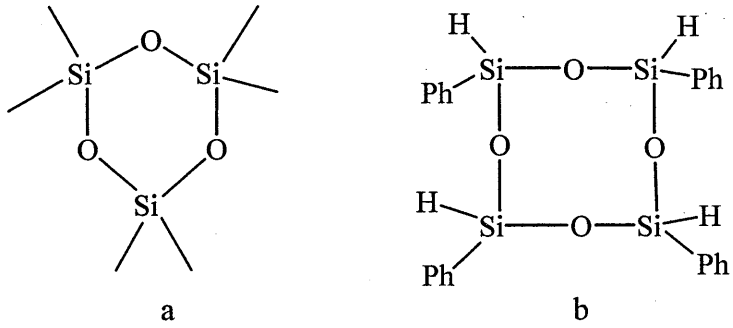


Figure 1.5

Siloxanes can also be arranged in cages usually based on T units. T cages are named in the same way as D units as shown in Figure 1.6.

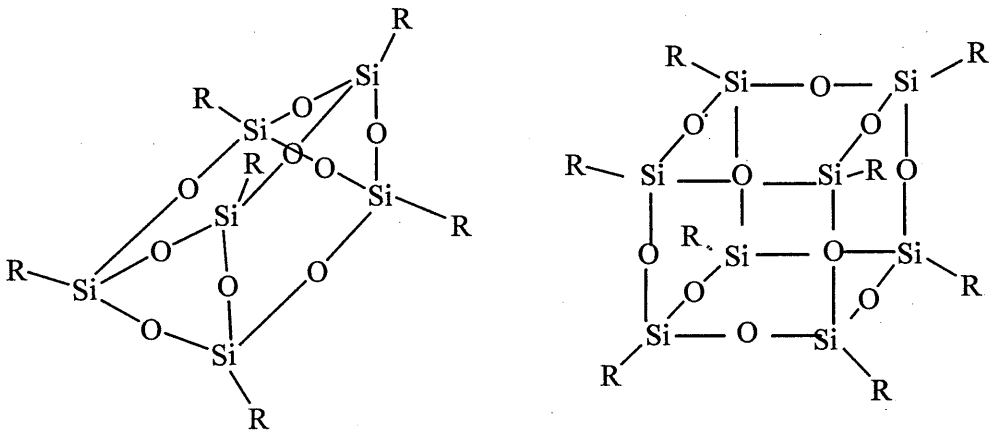


Figure 1.6 - Structures of T_6 and T_8

1.8 – Analytical and spectroscopic techniques for silicon containing compounds.

1.8.1 ^{29}Si-NMR Spectroscopy.

^{29}Si-NMR spectroscopy is the most important analytical technique for the analysis of organosilicon compounds[30] and silicates etc., because of its simplicity, the amount of

information gained and the non-destructive nature of the technique itself[31]. It was shown very early on that the isotope ^{29}Si is valuable for NMR spectroscopic analysis but several technical difficulties had to be overcome before silicon spectra could be recorded on a routine basis. The low sensitivity of the isotope ^{29}Si, its low abundance and the rather long relaxation times were the main reasons why ^{29}Si-NMR spectroscopy was not used earlier. Most of these problems, as well as the general problems encountered in proton or carbon NMR spectroscopy, were resolved by the introduction of the Fourier-Transform-Technique (FT-NMR spectroscopy).

The development of an understanding of the theory of ^{29}Si-NMR spectroscopy is important for two reasons:

1. Silicon is strategically located in the Periodic Table of the elements below carbon and, between aluminium and phosphorus. Thus silicon NMR spectroscopic values will be important in the development of a unified theory of chemical shifts and coupling constants of the heavier elements.
2. The normal coordination number of silicon is four. Two of the parameters used for the calculation of the paramagnetic component are bond orders and bond angles. Bond angles are rarely determined experimentally with high precision. Due to the coordination number four, a number of compounds exist in which bond angles are governed by symmetry.

1.8.2 - Detection of the ^{29}Si-NMR signal.

In nature silicon consists of three isotopes: 92.21% ^{28}Si, 4.70% ^{29}Si and 3.09% ^{30}Si; of these isotopes only ^{29}Si has a spin I=½ and a magnetic moment of μ=-0.961 nuclear magnetons. The properties of nuclei having a spin of ½ are well documented but the

fact that only a minor proportion of the silicon has a magnetic moment leads to particular problems.

In terms of the resonance condition, silicon can be compared to carbon. Both elements are members of the fourth group in the Periodic Table. One of the isotopes of carbon has a spin of ½, ^{13}C, with natural abundance even lower than silicon (1.1%). Thus it might be expected that ^{29}Si-NMR spectroscopy would be easier to perform than ^{13}C-NMR spectroscopy.

Although both elements belong to the same group of the Periodic Table, they reveal some small but important differences in their chemical behaviour. The content of carbon in organic compounds is usually higher than that of silicon in organosilicon compounds. For instance, the simplest carbon substituent is the methyl group but the simplest common silicon substituent is the trimethylsilyl group. Both groups contain one nucleus each of the isotope in question but the volume requirement of the latter group is about six times as large as that of the former with a proportionately weaker NMR signal.

Another problem arises from consideration of the spin-spin splitting with other magnetic nuclei. This is evident in the case of hydrogen containing compounds. Here the neighbouring N protons with I = 1/2 split the silicon resonance into N+1 lines. Applying a strong resonance frequency with a frequency around the resonance frequency of the protons, enables the spectrum to be simplified due to the removal of the splitting. Since the number of lines is now reduced to one, this should result in an improved signal to noise ratio.

As a result of the low natural abundance of silicon, together with its long relaxation time, the recording of ^{29}Si-NMR spectra usually takes a very long time. There are two ways to reduce the recording time for a ^{29}Si-NMR analysis: the first method involves

the addition of a small amount of a shiftless paramagnetic complex such as trisacetylacetonatochromium (III), $Cr(acac)_3$ (acac = acetylacetone), to the sample (with a typical concentration of 10^{-2} to 10^{-3} mol/l). This method has the advantage of reducing the relaxation times for silicon nuclei with different environments to relatively low values[32]. However this chemical additive is not completely shiftless[33] and may affect the chemical shift of sensitive chemical systems. Another disadvantage of using this method is that the sample cannot be easily recycled.

The other method of eliminating the NOE involves the use of pulse modulated decoupling, also called gated decoupling. No chemical additives are necessary and, in addition, the shortcomings of the former technique are avoided. However, because of the recovery time needed after each scan is completed, the build-up of the signal in the computer does take much more time. Thus, in spite of the great potential of ^{29}Si-NMR spectroscopy, before the advent of cheap computers, relatively few studies in this field were carried out.

1.8.3 – Chemical shifts in ^{29}Si-NMR Spectroscopy.

The chemical shift range of silicon compounds in ^{29}Si-NMR spectroscopy is very large between –180 ppm to 250 ppm. Thus ^{29}Si-NMR chemical shifts are very useful diagnostic tools. However, determining the electronic distribution at silicon from such techniques is difficult.

It is useful to compare the bonding states of silicon with other elements around it in the Periodic Table especially with carbon. As stated earlier, the coordination number of most silicon compounds is four. These types of substance correspond to alkane derivatives in carbon chemistry. Whilst compounds having a coordination number of less than four are common in carbon chemistry they are not common in silicon

chemistry; on the other hand, coordination numbers of five and six are not unusual in silicon compounds and this helps to explain the wide range of chemical shifts observed in silicon compounds.

Many factors can affect the chemical shifts in ^{29}Si-NMR spectroscopy. For example, strain can have a pronounced effect on the chemical shift of a silicon atom. Apart from siloxanes, only a limited set of different ring sizes is available. Ring strain can result in deshielding as well as shielding effects and it is not always possible to predict whether a change of ring size will give rise to greater or a smaller change in chemical shift.

In this thesis we will only consider siloxanes and in particular D rings and T units. In the final chapter we will also consider siloxane polymers as open chains. The chemical shifts of D rings and T units usually depend on the size of the molecule, and in particular the number of siloxane units in the molecule. In the case of D rings the chemical shift range is from –9 ppm (D_3) to –22 ppm (D_x with $x > 7$). The chemical shift of D_3, D_4 and D_5 is –9.9 ppm, -20.20 ppm and –22.80 respectively. The difference between the chemical shifts of D_3 and D_4 is larger than that between D_4 and D_5 and this is due to ring strain which has a greater affect the smaller the ring (the reason for this will be given in Chapter 2). The same pattern is observed in the case of T units.

The substituent on the silicon atom also affects the chemical shift; the presence of one or more phenyl group results in a shielding effect due to the different hybridisation of the carbon next to the silicon.

1.8.4 – Solvent effect.

Studies on ^{29}Si-NMR spectroscopy are normally conducted at the highest possible concentration, using either saturated solutions or liquids, but there are a few analyses of the effect of dilution caused by different solvents. The compound studied most thoroughly is tetramethylsilane (TMS), a common reference for ^{29}Si as well as for ^{13}C and ^{1}H. The measurement of the solvent shift of a 2 % v/v solution of TMS in a number of halogenated derivatives of benzene and cyclohexane reveal an additional shielding in benzene and deshielding in cyclohexane relative to pure TMS in a range of between –0.49 (C_6H_6) and –0.15 ($C_6H_{11}I$) due to magnetic anisotropy.

Relatively substantial dependencies on the donor number of a solvent have been observed for the ^{29}Si chemical shifts of silanols and silylamines.

1.8.5 – IR Spectroscopic analysis in organosilicon chemistry.

IR absorption bands arising from bond vibrations involving silicon atoms are about five times more intense than the bands from the corresponding carbon linkage. The reasons for this have been discussed by Wright and Hunter[48]. This fact helps considerably in the development and characterisation of organosilicon polymers and related materials. Extensive studies on such materials have been carried out by Young, Servais, Currie and Hunter[49], Richards and Thompson[50] and Clark, Gordon and Hunter[51].

The frequency of bands involving silicon appears to be largely unaffected by the physical state, except when hydrogen bonding is present. This was confirmed by Simon and McMahon[59] by comparing the spectra of some alkylsilanes and siloxanes in gaseous, liquid and solid phases.

Frequencies which have been suggested as being characteristic of specific groupings involving silicon, are listed in Table 1.3. The correlations listed have been supported by a considerable number of fundamental studies on single molecules or related groups, such as silanes[52,53], tetramethyl silanes[54,55], and methyl[62,63] and halogenated silanes[56,57,60,61,62].

Silicon grouping	Typical characteristic frequencies (/cm^{-1})		
$Si(CH_3)_3$	1260,1250	Near 840 and 755, 715-680, 660-435	
$Si(CH_3)_2$	1258±5	Near 850, and 800	
$Si(CH_3)$	1258±5	Near 765	
$Si(CH_2)$	1250-1200	760-670	
SiC_6H_5	1125-1100		
Si-O-Si	Cyclic	Trimers 1020-1010 Tetramers 1090-1080 Larger rings 1080-1050	
	Open Chain	1093-1076, 1055-1020	
Si-O-C		1110-1080	
SiH	Overall	2280-2050	
			Alkyl or Aryl
	SiH_3	Alkyl 2153-2142 Aryl 2157-2152	947-930, 930-910
	SiH_2	Dialkyl 2139-2117 Diaryl 2147-2130	
	SiH	Trialkyl 2105-2095 Triaryl 2132-2112	
SiF	1000-830		
Si-Cl	usually one at 600-550	Overall 650-370	

Table 1.3 – Absorption frequencies of Silicon-containing Groups (/cm^{-1}).

In this thesis the organosilicon compounds used were: silanes, siloxanes, halogenosilanes and silanols. The IR spectra of such classes of compound will thus be discussed here in more details.

Si-O stretching vibration. The Si-O-Si bond gives rise to at least one very intense band in the 1100-1000 cm^{-1} region due to an anti-symmetric stretching mode. However, the corresponding mode of the Si-O-C group also appears in this region so that the two cannot always be differentiated. In the case of polymeric siloxanes, only Si-O-Si units are present unless the silicon atom has an alkoxy substituent. There are clear differences between cyclic and open chain polysiloxanes which reflect the differing bond angles.

Cyclic siloxanes. Wright and Hunter[48] have reported the spectra of cyclic materials from hexamethylcyclotrisiloxane to hexadecamethylcyclo-octasiloxane. In the trimer the Si-O band appears at 1018 cm^{-1}, whilst in the remainder it falls in the range 1076-1056 cm^{-1}, the frequency showing a small but steady fall throughout the series with increasing ring size. Richard and Thompson[50] confirmed these findings for the first five members of the series, and also examined two cyclic aromatic siloxanes $(SiPh_2O)_3$ and $(SiPh_2O)_4$. The first of these materials gave a strong band at 1015 cm^{-1} close to that of the trimer of the methyl series, whilst the tetramer gave its strongest band in the region nearer to 1100 cm^{-1}.

Young at al.[49] studied the trimers and tetramers only, but covered a wide range of substituents on the silicon atom such as dimethyl, diethyl, diphenyl, methyl–phenyl and ethyl-phenyl. They found that there is remarkably little difference in the position of the Si-O-Si absorption bands with variation in the nature of the substituent, although there was a considerable shift on going from the trimers to the tetramers. They found all the trimers to exhibit an Si-O-Si absorption band in the narrow range 1020-1017 cm^{-1}, whereas all the tetramers absorbed in the range 1093-1081 cm^{-1}.

The ability to distinguish between trimers and tetramers in this way is valuable as these are the most commonly produced cyclics from the hydrolysis of chlorosilanes.

The occurrence of only one strong band in this region is also diagnostic, since open chain polymers usually have two bands, except in cases where the chain is branched.

Open-chain polymeric and monomeric siloxanes. In the series of open chain polymethylsiloxanes from hexamethyldisiloxane to octadecamethyloctasiloxane, Wright and Hunter[49] found the Si-O absorption falls in the range 1055-1024 cm^{-1} and again there is a small decrease in the frequency for each unit increase of the chain length. However this band is accompanied by a second strong band between 1093-1076 cm^{-1}, the frequency now rising with the degree of polymerisation.

Silanols have been reported[64,65] to give bands at 900-885 cm^{-1} with lower values near 820 cm^{-1} for aromatic silanols.

Si-H stretching vibrations. In silane itself, the Si-H stretching frequency[52,53] is at 2187 cm^{-1} and this fixes the approximate region in which this group can be expected. In fact the stretching frequency is very sensitive to the electronegativity of the groups attached to the silicon atom, so that trichlorosilane[58] absorbs at 2274 cm^{-1} whereas trimethylsilane absorbs at 2118 cm^{-1}.

A number of trisubstituted silanes with three identical sustituents have been studied by Smith and Angelotti[66] to examine the dependence of the Si-H stretch on electronegativity. Additional data is available from studies on siloxanes and similar materials. The effect of the electronegativity of the substituents on the frequency of Si-H vibration is demonstrated by the values of the trifluoro (2282 cm^{-1}) tribromo (2236 cm^{-1}) and trimethoxy (2203 cm^{-1}) silanes.

Si-OH vibration. The free OH stretching frequency of silanols is significantly higher than that of methanol. This is consistent with the usual rise in OH frequencies when the oxygen atom is attached to an element with low electronegativity. The free OH frequencies of alkyl and aryl silanols have been examined by West and Baney[67, 68] and

by Nillius and Kriegsmann[69]. The aryl compounds absorbs at slightly lower frequencies than the alkyl compounds. Whilst this difference is only about 11 cm^{-1} there are large differences in the acidities and basicities of the two compounds[67,68]. In cyclohexane solution, trimethylsilanol absorbs at 3697 cm^{-1} and the triaryl compounds at 3686 cm^{-1}. Mixed derivatives show intermediate values. Both compounds are sensitive to solvent effect.

In the liquid state these compounds associate in the usual way and the OH frequencies fall to about 3250 cm^{-1}. The values depend, of course, upon the hydrogen bond strengths, and the band broadens and intensifies, as in normal alcohols.

1.8.6 – Mass Spectrometry: The MALDI-TOF technique.

Mass spectrometry is a valuable technique for the characterisation of siloxane compounds. Whilst mass spectrometry gives the molecular mass of the molecule, the fragmentation gives an opportunity (together with other analytical techniques) to understand the structure of the siloxane compound. The majority of compounds analysed in this thesis have a very high molecular mass and therefore conventional mass spectrometry could not always be used. For this reason the MALDI-TOF (Matrix-Assisted Laser Desorption/Ionization Time of Flight) technique was particularly useful.

In early applications of lasers in mass spectrometry, the neat analyte (no matrix) was irradiated directly with an intense pulse of laser light for a short time[70-78]. Energy transfer to the analyte was achieved with lasers emitting in the UV range to cause electronic excitation or in the IR region to cause vibrational excitation and ionisation of the analyte. Direct laser desorption had a limited application and was effectively

substituted by the matrix-assisted desorption/ionisation (MALDI) technique in the late 1980s.

In this technique, the sample is mixed into a solution of a liquid or more often a solid matrix to achieve a molar ratio of analyte to matrix in the range of 1:100 to 1:50,000[79-88]. The matrix is selected for its laser energy absorption properties, thus avoiding sample decomposition, and its solubility characteristics, which are usually chosen so they are similar to those of the analyte.

The operating principles and a typical configuration of a MALDI instrument with a time-of flight (TOF) mass spectrometer are illustrated in Figure 1.7:

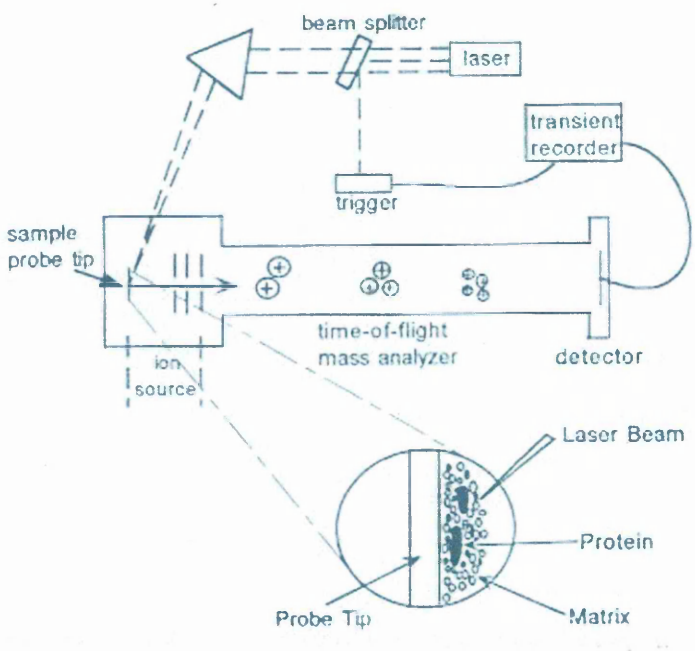


Figure 1.7 –Representation of a typical MALDI-TOF instrument with a protein as analyte in excess of matrix[154].

The sample and the matrix are mixed together in an organic solvent of mutual solubility; the solvent is then removed and the mixture of analyte and matrix co-precipitated onto a sample planchet. The matrix must have certain properties to be

suitable for such analysis[89-98]: (1) the matrix molecules must have a high adsorptivity for the laser radiation and (2) the matrix must be capable of forming a fine crystalline solid during co-decomposition with the analyte. Figure 1.8 shows some molecules commonly used as the matrix.

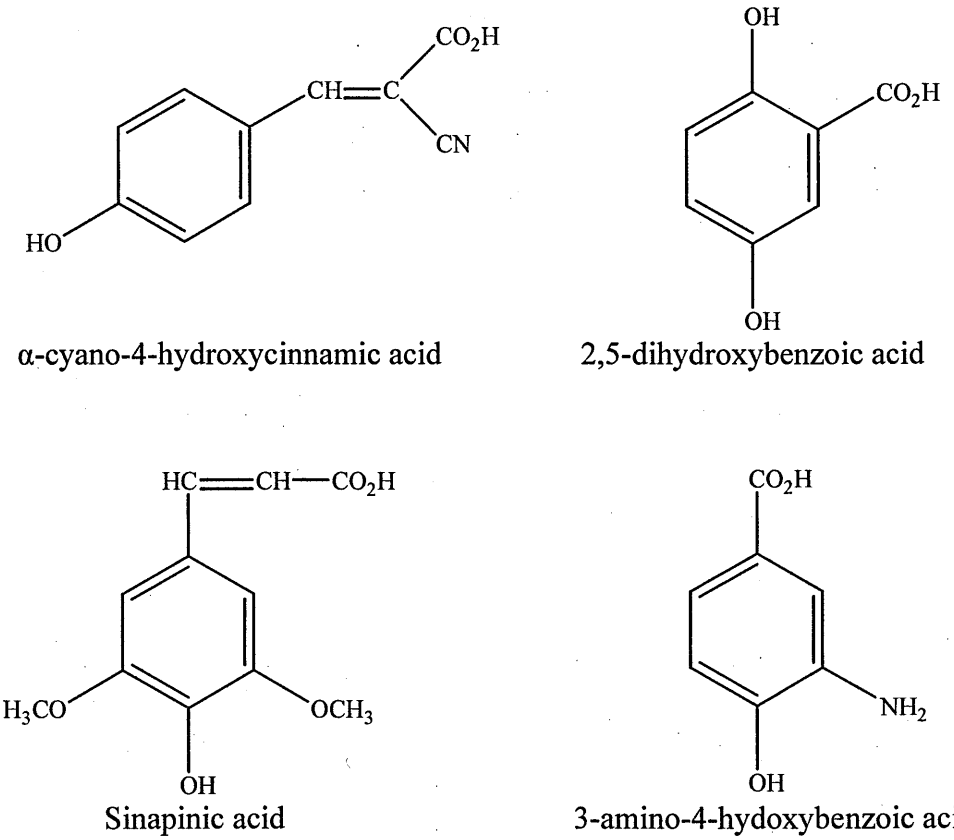


Figure 1.8 – Some of the molecules commonly used as matrix.

The suitability of a matrix compound for MALDI is dependent not only on its capacity to absorb radiation from the laser but also on its capacity for decomposition as described by Liao and Allison[99].

The more homogeneous and fine-grained the morphology of the crystal formation within the matrix, the more intense is the MALDI mass spectrum of the analyte[100-103].

The mechanism for ionisation of the analyte during MALDI is not completely understood however[104-109]. Liao and Allison[99] discovered that proton transfer from a matrix molecule to the analyte appears to be involved in the ionisation step[99]. The proton that is transferred to the analyte may be derived from a photoionized or an electronically excited matrix molecule[107]. Thus, the most significant peak in the MALDI mass spectrum usually represents the protonated molecules of the analyte.

The early resolving power[110-111] of a typical linear TOF mass spectrometer was below m/z 1000. It has been increased to m/z 2000 and even greater values have been obtained with a reflectron. Because of the problem of resolution, it is important to avoid contaminants that have a molecular mass close to that of the analyte of interest. Despite the poor resolving power, the mass accuracy is remarkably good but often it is not possible to discern the presence of individual isotopic peaks. In MALDI-TOF mass spectrometry, the peaks observed represent an average distribution of the isotopic composition and mass of the ions they represent.

The great virtue of MALDI is its capacity to form protonated molecules of large, involatile compounds and to measure the mass (± 0.01%) to a relatively high accuracy. For this reason, MALDI-MS instruments are frequently thought of as "molecular weight machines". As relatively little or no fragmentation is observed in conventional MALDI-MS, structural information must be obtained from specialised instrumental techniques or from degradation or modification of the analyte and subsequent reanalysis.

Because of its capacity to analyse molecules with large molecular weight, MALDI has been used extensively in the structural characterisation of proteins[112-114] often after isolation by two-dimensional electrophoresis[115-116]. Other applications include confirmation of sequences of recombinant proteins[117], comparison of homologous

proteins from different tissue[118] and also analysis of non-biological polymers, as used in industry[119-130]. Other innovative developments include the on-line combination of MALDI with chromatography[131-136] and its application to quantitative analysis[137-138].

CHAPTER 2

"NON AQUEOUS" HYDROLYSIS OF

DICHLOROSILANES – SYNTHESIS OF D_3

2.1 - The aim of the present work.

Cyclic siloxanes constitute an important class of silicone polymer precursor because one of the most important methods for preparing high molecular weight polysiloxanes is the ring-opening polymerisation of such cyclic monomers.[35] In the present work, we propose to use non aqueous hydrolytic methods to form cyclic siloxanes using various high oxidation state compounds as the source of oxygen.

Based on this we hope to:

i) develop a high yielding route to cyclic siloxanes.

ii) optimise conditions so that it is possible to obtain preferentially D_3 and other rare cyclics in a quantitative, and possibly, selective fashion.

iii) extend the method to the selective production of resins and cages from $RSiCl_3$.

iv) understand the mechanism of such "non aqueous" hydrolysis.

2.2 – Preparation of siloxanes by non-hydrolytic reactions. Previous work.

The D_3 ring is not easily formed by aqueous hydrolysis of dichlorosilanes below 150 °C because of its ring strain. Under these conditions D_4 is the thermodynamically favoured cyclic compound. Thus, the development of a method for primarily producing D_3 would be advantageous. To achieve this, D_3 would need to be the kinetically favoured product.

Water is the conventional source of oxygen for siloxane formation. Non-aqueous siloxane formation requires compounds that contain oxygen that can be readily donated to the silicon.

Diphenylsulfoxide has been shown to react with chlorosilanes to give siloxanes, as reported in a French Patent in 1966[161a] by John Goossens from the General Electric Co., who transformed a chlorosilane into a silanol according to Equation 2.1.

$$R_2SiCl_2 \xrightarrow{DMSO} R_2Si(OH)_2$$

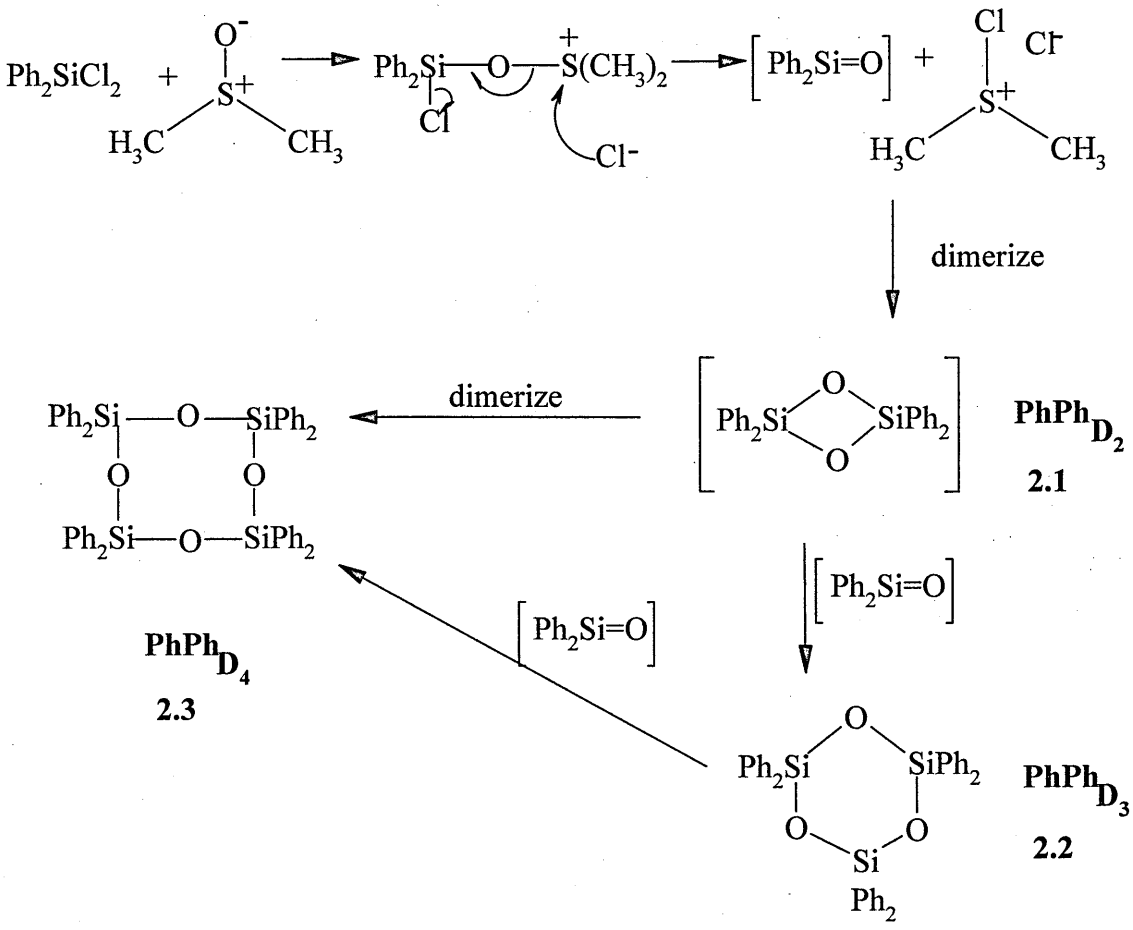
Equation 2.1

The silanol undergoes subsequent condensation to give siloxanes, in particular D_3. Goossens also studied the reaction of Ph_2SiCl_2 with DMSO in the non-polar solvent, heptane, at a temperature of 60°C. The product obtained was a mixture of hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane in yields of 91% and 8% respectively. Both products were solid and therefore easily isolated by treatment with methanol.

Under similar conditions, Goossens reacted $PhMeSiCl_2$ with DMSO. The products obtained were again a mixture but, this time, the cyclotrisiloxane was also a mixture of *cis* and *trans*-triphenyltrimethylcyclotrisiloxane (65%) with the major component being the *trans* isomer (81.5% *trans*; 18.5% *cis*), together with 30% of the mixed cyclotetrasiloxane. According to the patent, the presence of a methyl group decreased the melting point dramatically and in fact all the products were oils (the yields were calculated by gas-phase chromatography).

2.2.1 – The Weber-Voronkov mechanism.

This reaction has been rediscovered by many workers such as Voronkov and co-workers[187], Weber and co-workers[188] and Brook and co-workers[189]. Weber and Voronkov proposed a mechanism involving a silanone as an intermediate, as shown in Scheme 2.1.

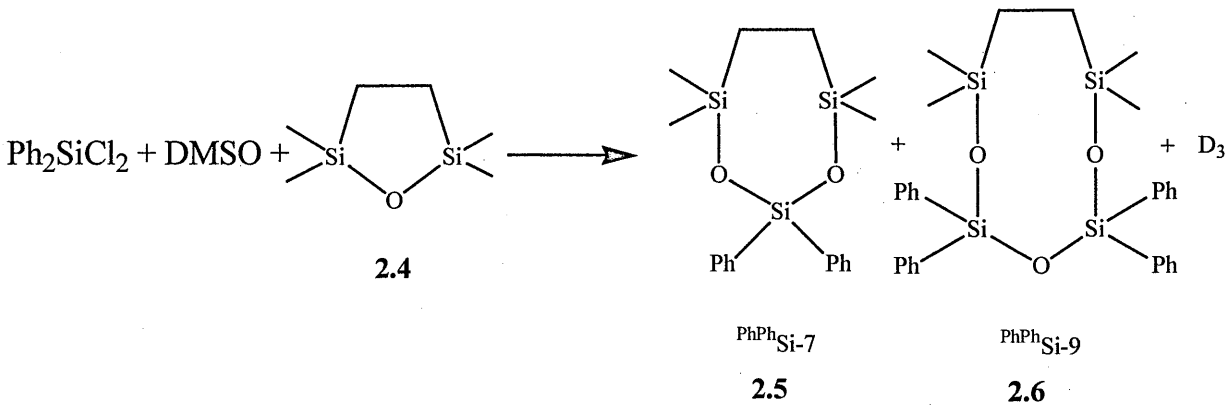


Scheme 2.1- The mechanism proposed by Voronkov involving a silanone.

According to this mechanism, siloxane formation is a result of polymerisation of the silanone intermediate. Later studies made by Weber[188] suggested that the first step of the polymerisation is the formation of the dimer, which is particularly unstable due to its high angle strain. Kudo and Nagase[208] calculated the Si—O—Si and the O—Si—O angle in the dimer to be 88.5° and 91.5° respectively. However, we believed that the mechanism proposed by Voronkov seemed to be very unlikely, since silanones are very high energy species and are only observed when bulky substituents are attached to the silicon. Voronkov[198] provided evidence for the generation of a silanone in a later paper where he generated the silanone in a different way by the reaction of a hexamethyldisiloxane with gallium halides which rearranged to form the silanone and halosilane.

2.2.2 – The controversial matter of the silanone.

The work reported by Weber seemed to support the mechanism proposed by Voronkov. According to Weber's paper, published in 1996, the silanone generated by reaction of Ph_2SiCl_2 and DMSO could react *in situ* with 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (**2.4**), as shown in the Scheme 2.2, to form



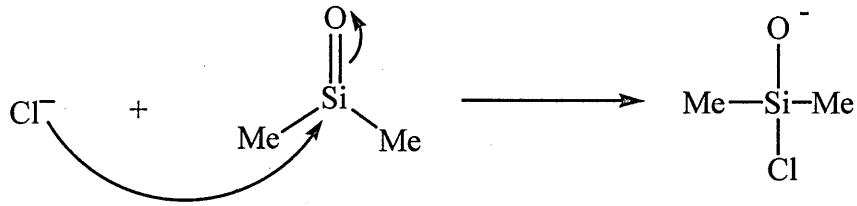
Scheme 2.2

4,4,7,7-tetramethyl-1,3-dioxa-2,2-diphenyl-2,4,7-trisilacycloheptane (^{PhPh}Si-7 **2.5**), 6,6,9,9-tetramethyl-1,3,5-trioxa-2,2,4,4-tetraphenyl-2,4,6,9-tetrasilacyclononane (^{PhPh}Si-9 **2.6**) and D_3.

Weber came to the conclusion that ^{PhPh}Si-7 was formed by the reaction of the silanone with **2.4** and ^{PhPh}Si-9 was formed either by a further reaction of ^{PhPh}Si-7 with another molecule of silanone or by reaction of **2.4** with the dimer (cyclic D_2). This latter route was supported by the fact that the separate reaction of ^{PhPh}Si-7 with silanone (produced from the mixture of Ph_2SiCl_2 + DMSO) did not give ^{PhPh}Si-9.

We believe that these results have a different interpretation. If the silanone were an intermediate, it will be formed along with the dimethylchlorosulfonium/

chloride ion pair. As Weber himself admitted, the silanone is a very reactive species, thus is likely to react with the Cl^- of the sulfonium salt as in Scheme 2.3, leading to the chlorosilanolate intermediate. As we shall discuss later, this is the more likely intermediate, and the one proposed by Brook.



2.7

Scheme 2.3

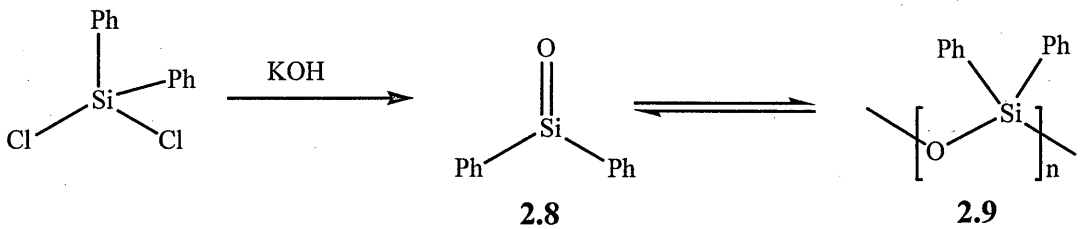
A further consideration comes from the second reaction performed by Weber and reported in the same paper, namely the reaction of ^{PhPh}Si-7 + Ph_2SiCl_2 + DMSO wherein no ^{PhPh}Si-9 was formed. Weber reported that ^{PhPh}Si-7 is not sufficiently reactive to form ^{PhPh}Si-9 but the silanone is reactive enough to insert itself in the 2,5-disilacyclopentane (**2.4**). Assuming again that the formation of silanone is real, if it does not react with ^{PhPh}Si-7 it would dimerise almost immediately and subsequently form at least ^{PhPh}Si-11 by insertion of the dimer in ^{PhPh}Si-7 but this compound is not mentioned in Weber paper.

As mentioned earlier we believe in an alternative mechanism, where a linear α,ω-dichlorosiloxane is formed as the intermediate. We think that the only reason why ^{PhPh}Si-9 is not formed is because the α,ω-chlorosiloxane proposed by Brook, is sufficiently stable not to react with a highly stable molecule like ^{PhPh}Si-7.

2.2.3 – Silanones.

Silanones are of particular interest for historical, commercial and theoretical reasons. Kipping coined the name *silicone*, by analogy with a ketone, because he believed the product of reaction of Ph_2SiCl_2 with base contained a silicon-oxygen double bond[43] (**2.8**).

It was noted shortly thereafter, by him and others, that the behaviour of the products was inconsistent with small molecules[44]. We now know that the silicones are linear and/or cyclic polymers (**2.9**); the equilibrium shown in Scheme 2.4 lies far to the right and it just such an equilibrium that forms the basis of the silicone industry:



2.8 **2.9**

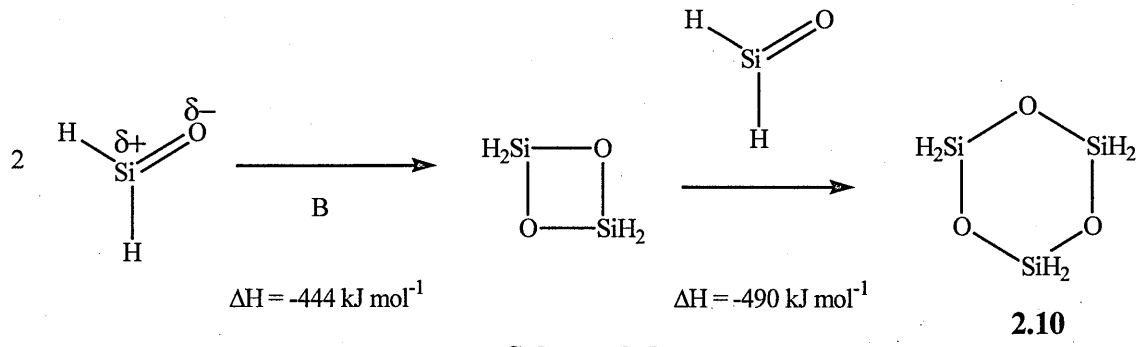
Scheme 2.4

However the generation of silanones as intermediates in the formation of siloxane rings, is still controversial. As already mentioned, due to their instability, silanones remain one of the few silicon based reactive intermediates for which kinetically stable examples have not been prepared. The only method to detect the presence of silanones consists of trapping them in a inert matrix, although the presence of bulky groups on the silicon does increase their lifetime. Infra-red analyses have been reported in the literature for some silanones such as difluoro[211] and dichloro-silanones[212], dimethyl silanone[213], methylsilanone[213], and silanone[213].

The strongest evidence for the formation of silanones comes from Davidson and co-workers[207] who described the thermolysis of D_4. This reaction leads to D_3 and D_5 suggesting that, in the thermolysis, the rate determining step is the decomposition of D_4 to give D_3 and methylsilanone which can react with D_4 to give D_5. Again, this evidence comes from experiments under extreme conditions such as the use of high temperatures.

Silanones are very likely to be highly polarised species that have a planar structure such that one end of the silanone is completely exposed. Due to the planarity around the Si—O

bond, the silicon is also more accessible to nucleophilic attack. The reactivity of the silanone bond has been calculated to be extremely high, as shown in Scheme 2.5:

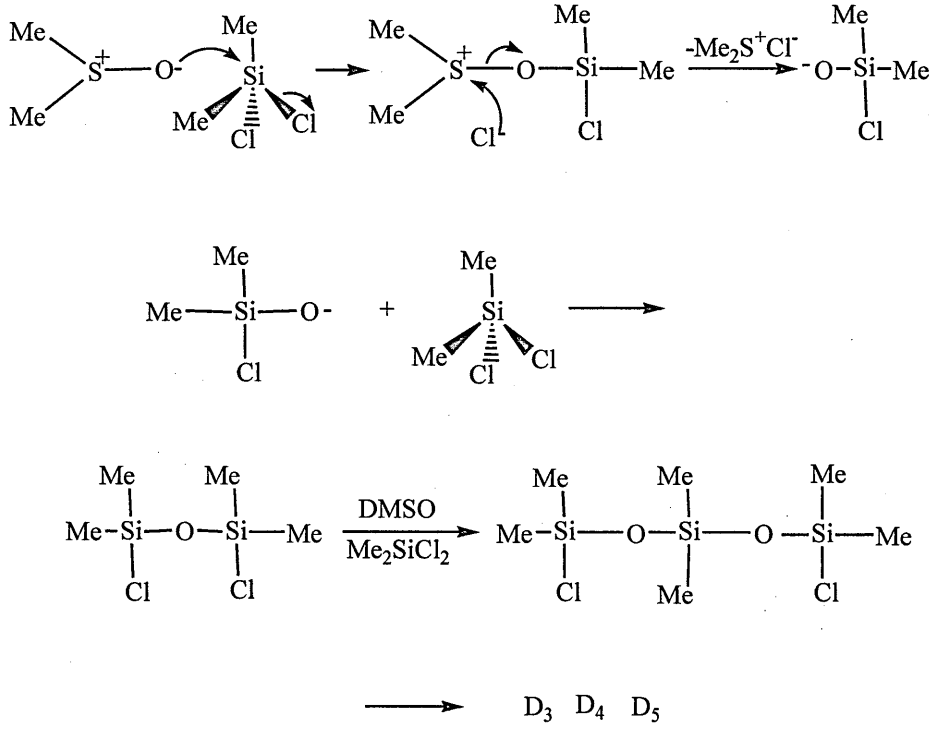


2.10

Scheme 2.5

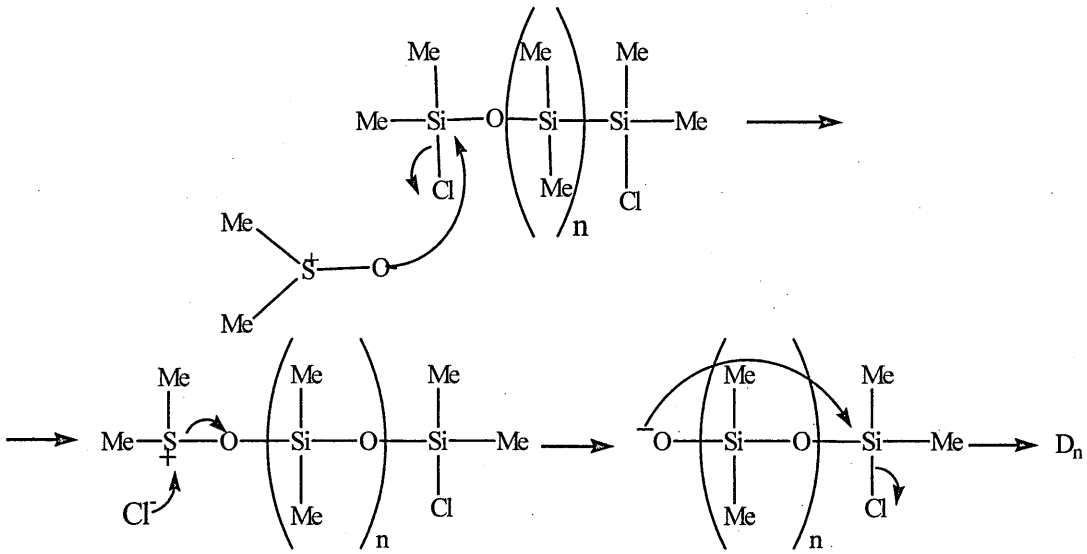
2.3 – An alternative mechanism for "Non-aqueous hydrolysis".

A different mechanism than that proposed by Voronkov, has been proposed by Brook and co-workers[160]. According to these researchers α,ω-dichlorosiloxanes are the intermediates involved in cyclic siloxane formation, as shown in Scheme 2.6.



Scheme 2.6 - Mechanism proposed by Brook involving α, ω-dichlorosiloxanes.

Cyclic siloxanes are formed via an intramolecular nucleophilic attack as shown in Scheme 2.7.



Scheme 2.7

As in the aqueous hydrolysis reaction, D_3 is not the only cyclic reaction product, other cyclic siloxanes, such as D_4, D_5 and D_6, are also formed. D_3 formation over the first half hour was monitored by Brook using ^{1}H-NMR. By plotting the formation of the cyclic siloxanes together with the disappearance of Me_2SiCl_2, it is possible to see that, during this time, D_3 is the main initial reaction product (for further details see Section 2.6 on page 62). Brook suggests that D_3 formation arises from the cyclisation of the 1,5-dichlorotrisiloxane. This suggests that a selective synthesis of the 1,5-dichlorosiloxane followed by its subsequent cyclisation with DMSO should give exclusively D_3. Unfortunately, the preparation of a large quantity of 1,5-dichlorotrisiloxane, is a difficult task, since the maximum yield obtained by Brook, from Me_2SiCl_2 using water or DMSO, was only 15%.

2.4 – The present work.

Our first step was to optimise Brook's conditions* so that it was possible to obtain D_3 quantitatively and selectively. Starting with Brook's original conditions, the reaction was monitored by GC and quantitative calculations made using an internal standard. The internal standard chosen was biphenyl, because, to be a good internal standard, it should not react with any of the reagents or with the solvent and have a convenient retention time. Biphenyl seemed to be an excellent choice in these respects. It also had a retention time that did not overlap with any of the product peaks.

2.4.1 – Speculation on the reaction of DMSO with Me_2SiCl_2.

As mentioned earlier, Brook followed the reaction of DMSO and dichlorosilane by NMR. In our group it was decided to follow this reaction by gas-chromatography. The first approach was, therefore, the analysis of the starting materials and the possible reaction products by GC in order to identify their retention times and also to find the appropriate GC program to avoid the overlapping of peaks. This was not difficult as the expected products D_3, D_4 and D_5 are commercially available.

A small amount of each of the products was dissolved in 1 ml of chloroform, chosen as solvent for the reaction, and injected onto to the GC separately using an isothermal program with a column temperature of 200 °C.

* This was based on Brooks earlier paper, since this work was done before the 1998 paper.

Under these conditions all the products were well separated except the dimethyldichlorosilane which overlapped with the solvent. Furthermore, the reaction products, the D rings, had retention times close to each other. It was then decided to use a chromatography program that started with a low temperature to allow the chlorosilane to be separated from the solvent followed by an increase in the temperature with time. After several attempts it was found that the best results were obtained using the following program: starting at 40 °C increasing the temperature at 1 °C/min up to 150 °C then maintaining this temperature for 5 minutes.

Using this program we were able to observe a good separation of both starting materials and products. Table 2.1 reports all the retention times of the starting materials, including the oxygen donors, and the reaction products:

Starting material	Product	Retention time (min.)
Me_2SiCl_2		1.83
DMSO		2.07
Pyridine N-oxide		not detected
Iodosobenzene		not detected
Trioxysulfurpyridine complex		not detected
Triphenylphosphine oxide		not detected
	D_3	3.81
	D_4	6.90
	D_5	9.61

Table 2.1 – Retention times of starting materials and products in chloroform.

The only products we were unable to identify by comparison with a standard sample were the by-products obtained from the oxygen donors, such as the α-chlorodimethyl-thioether

obtained from DMSO but, as they gave only one peak on the GC they were assigned by a process of elimination.

A standard solution was prepared using 0.54 mmols of each D ring dissolved in 5 ml of chloroform and the solution injected onto the GC. This solution was kept as a standard and injected every day, before starting any experiment, in order to check for variation of the retention times when the GC was turned off and to check that no degradation of the column occurred with time or with solvent. After several months no such decomposition was observed, giving an overall change of less than 30 s in the retention times of D_3, D_4 and D_5.

2.4.2 – Test runs.

The next step of the study was to verify whether the oxygen donor compounds could perform the "non aqueous" hydrolysis of cholorilanes. All the reactions were performed in chloroform and analysed by ^{29}Si-NMR and gas chromatography after 2.5 h. The presence of three peaks in the D region and in particular ^{29}Si-NMR peaks at δ= -19.02 ppm, δ= -21.46 ppm and δ= -22.13 ppm confirmed that all the oxygen donor compounds used formed D rings. This result was also confirmed by injecting the reaction mixture onto the GC giving peaks with retention times of 3.81 min, 6.90 min and 9.61 min. During the addition of the solution containing DMSO to the solution containing the dichlorosilane, an increase in the temperature of up to 45 °C was observed. The GC analysis revealed that D_3 was formed after a few seconds and its concentration decreased rapidly after a few minutes. In fact, the first injection, sampled straight after mixing the two solutions (30 – 40 s later), showed a similar concentration of D_3, D_4 and D_5 to that obtained after 3 min (this fraction was withdrawn, placed in a test tube in liquid nitrogen in order to stop the reaction proceeding, and then injected onto the GC when the programme was reset). The

chromatograms showed only a small amount of D_3 and almost an equal amount of D_4 and D_5.

These results confirmed that this reaction was very rapid at (or above) room temperature and, under such conditions, it was difficult to analyse. It was then decided to cool the reaction mixture using liquid nitrogen to –40 °C and to let the solution gradually reach room temperature. Analysis of the reaction mixture during this time allowed us to observe the variations in the concentration of the D rings with time.

2.4.3 – Calibration of the GC.

Two or three standard solutions with a known concentration of D_x or dimethyldichlorosilane and standard were prepared and injected onto the GC. The area of the standard and the area of the compound were measured for every injection. The calculations of the response factors were carried out as described in the following section. The Response Factors varied little from injection to injection or with standard solution. The value used in subsequent calculations was the average of all the determinations.

2.4.4 – Calculation of the response factors in the GC analysis.

All response factors were determined using pure compounds. The response factors were calculated using three freshly made solutions of different concentrations of pure sample X and pure biphenyl in chloroform. The three solutions were injected three times onto the GC column. Three chromatograms were obtained for each solution giving a total of nine chromatograms for each compound; for each chromatogram the corresponding response factor, K for the sample X was calculated according to the following relationship:

$$K = \frac{\text{area standard} \times \text{mols concentration (X)}}{\text{area X} \times \text{mols concentration standard}}$$

A typical plot of mmols of X vs $\frac{\text{area X x mols concentration standard}}{\text{area standard}}$ is shown in Figure 2.2. This is a straight line with the slope equivalent to the response factor (correlation coefficient $R^2 = 0.987$)

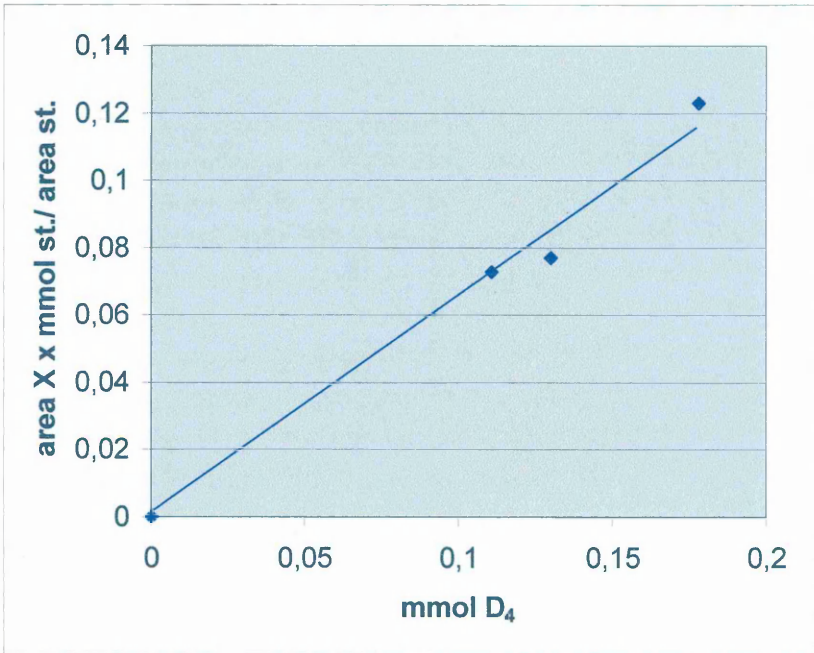


Figure 2.2 – Typical plot for D_4. In this case adamantane was used as standard (see later for discussion of why we changed from biphenyl to adamantane).

The area of the standard and compound X are obtained from the integration of the chromatogram and the molar concentration calculated from the weighings. The response factor used was the average value obtained from all the injections. This procedure was used for the calculation of the response factor of D_3, D_4 and D_5.

Table 2.2 summarises the response factors for all the reagents and products for which we had pure samples and for the different standards used:

Reagent and product	Response factor (Biphenyl)
Me_2SiCl_2	5.57
D_3	2.89
D_4	1.69
D_5	1.35

Table 2.2 – Response factors of reactants and products using biphenyl as a standard.

The quantity in mmols of the D_3, D_4 and D_5 rings in the unknown reaction mixture were then calculated using the relationship:

$$\text{mmol X} = \frac{\text{area X x mol standard}}{\text{area standard x}} \text{ x K}$$

2.5 – "Non aqueous" hydrolysis of dimethyldichlorosilane.

2.5.1 - Me_2SiCl_2 + DMSO.

This reaction was performed using $CHCl_3$ as the solvent and a ratio of Me_2SiCl_2 to DMSO of 1:1. Half of the solvent was used to dissolve the dichlorosilane and to this solution was added the DMSO dissolved in the second portion of solvent.

The reaction between DMSO and Me_2SiCl_2 is an exothermic reaction, so both solvent and reagents were cooled to -30 °C. Once the reaction was started it was allowed to warm to room temperature. The reaction mixture was sampled at various times and immediately injected onto the GC so that the amounts of the reaction products, D_3, D_4 and D_5 could be calculated. Figure 2.3 shows the results obtained from plotting the amounts of D_3, D_4 and D_5 versus time.

As expected the concentration of the starting material decreases in a steady fashion. The diagram shows an initial increase in D_3 and D_4 followed by a subsequent decrease in the amounts of these products, especially D_3. The mass balance is not reported in the graph because D rings larger than D_5 are expected to be formed but they will not be detected by

the GC due to their long retention times. These larger rings were also not detected by ^{29}Si-NMR possibly because the large D rings gave a broad peak.

	Amount of material/mmol			
Time /h	Starting Material/mmol	D_3	D_4	D_5
0	9.14	0	0	0
1	2.82	1.43	0.83	0.36
2	0.54	2.72	2.38	0.73
3	0.17	1.93	2.72	0.76
4	0.09	0.71	1.80	0.76
5		0.26	2.41	0.97

Table 2.3- Comparison of the amount of product with the starting material. Analysis with the time for the reaction with DMSO.

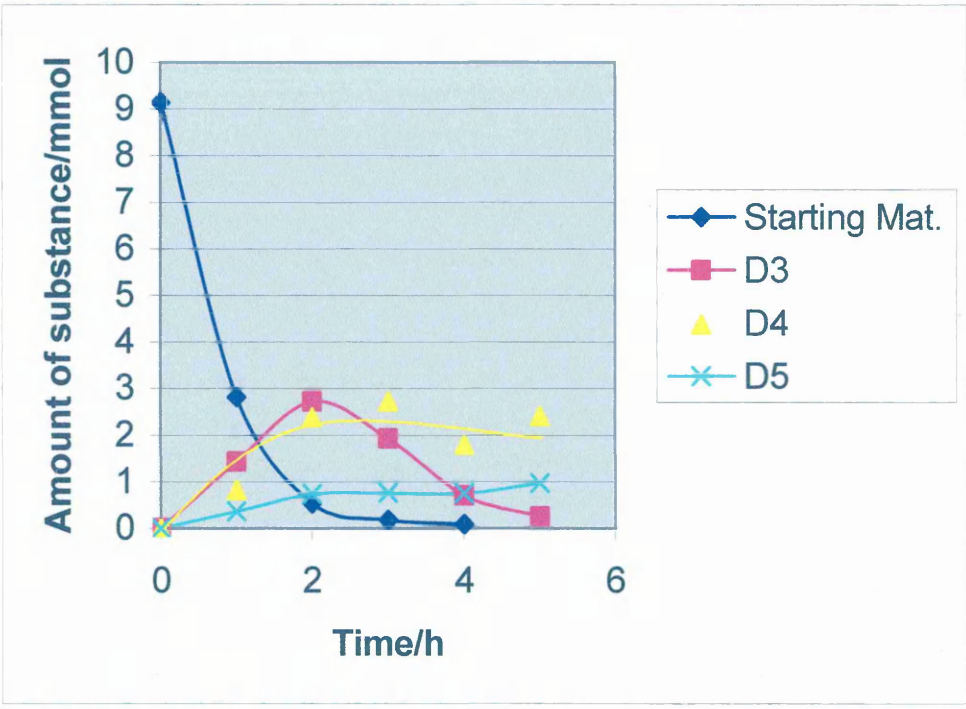
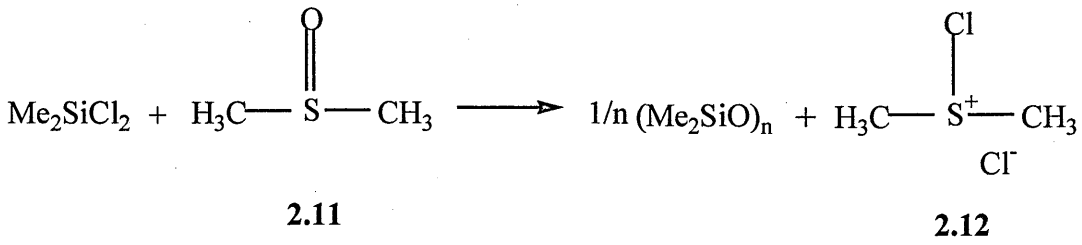


Figure 2.3 – Reaction products for DMSO + Me_2SiCl_2 vs. time.

The overall equation for this reaction is:



2.11 **2.12**

Scheme 2.8 – Formation of D_n.

During the reaction we also observed GC peaks for CH_3—S—CH_2Cl (**2.13**) (due to a spontaneous rearrangement of **2.12** and CH_3—S—CH_3 formed by loss of chlorine. However, it was not possible to quantify their formation, because it was not possible to determine their response factors. However it was clear that their increase mirrored the rate of loss of Me_2SiCl_2 starting material confirming that the first step is the reaction of the DMSO with the monomer.

Clearly the scatter on the points in Figure 2.3 arises from experimental error and, in particular, the way in which the integrator interprets the peaks. However, the general trend is clear, the amount of D_3 increases first, then decreases, as larger rings are formed. Brook also observed a similar pattern, suggesting that D_3 is an intermediate that is subsequently converted into D_4 and D_5 in the presence of the oxygen donor compounds. Thus, in order to obtain the highest yield of D_3, it is necessary to quench the reaction as early as possible and inhibit the subsequent rearrangement to D_4.

Interestingly there appears to be a rapid reaction on addition of the reagents if the reactants are not cooled. Monitoring the mixture by GC. in the early part of the reaction showed a loss of the starting material even after 3 min. This is not caused by aqueous hydrolysis arising from fortuitous water in the solvent or on the column. This was confirmed by repeating the reaction in the absence of DMSO. The involvement of DMSO in this initial

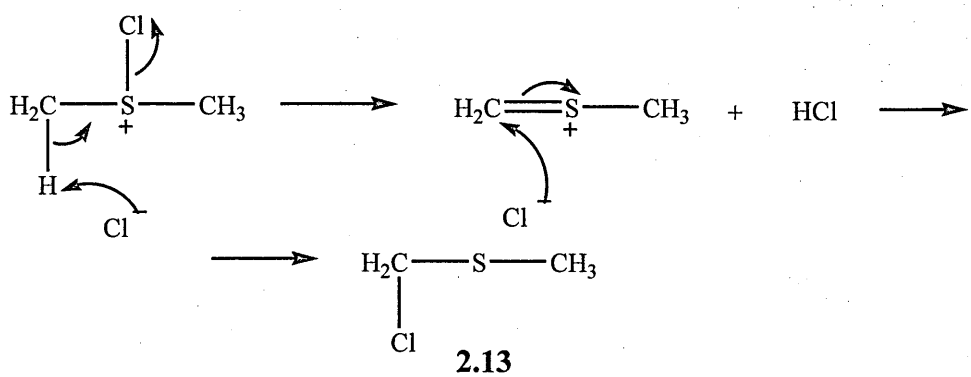
burst is also shown by the corresponding increase in the peaks arising from CH_3—S—CH_2Cl (**2.13**) and CH_3—S—CH_3.

2.6 - Comparison between Brook's data and the results obtained in this work.

When this Ph.D. work was started in November 1997, Professor Brook and his co-workers had not yet published the results of their NMR work. This did not appear until in May 1998 and therefore the results of the experiments performed in their laboratory were not known to us.

According to Brook's paper the reaction was carried out in the absence of solvent[189]. The ratio of DMSO to methyldichlorosilane was 1:1 but the DMSO was added in five aliquots of 1/5 of the total, every 15 min for a total reaction time of 75 min. Before every addition he recorded a ^{1}H-NMR. Thus there are some differences between Brook's methodology of performing this reaction and the method we used in our laboratory.

Firstly, the absence of solvent; in our laboratory the reaction was performed in chloroform and, as stated earlier, the reaction was highly exothermic. In his paper Brook mentions the formation of a crystalline product which was attributed to the chlorodimethylsulfonium chloride. In our experiment no crystalline product was observed probably because we used a slightly polar solvent in which the sulfonium salt could dissolve. The sulfonium salt was not detected by GC although we did observe a further peak with a retention time similar to the solvent and the chlorosilane. We assumed that the sulfonium salt would decompose at the high temperatures in the GC, probably being converted into the α-chlorodimethylthioether as shown in Scheme 2.9:



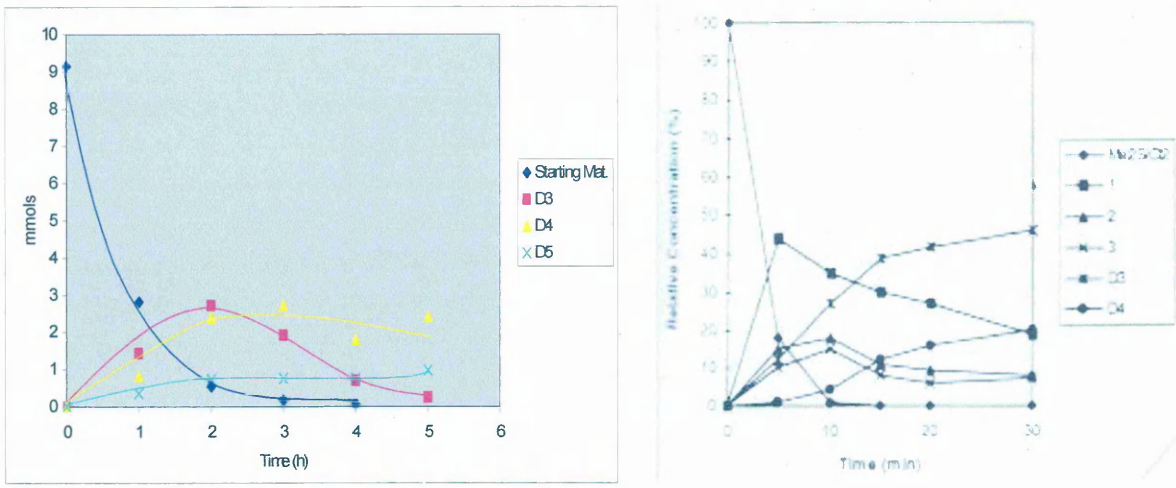
2.13

Scheme 2.9 – Proposed mechanism of decomposition of the sulfonium salt.

The addition of the two reagents at once and the consequent increase in the temperature led to a very fast reaction. Unlike Brook's observation, no linear α,β-dichlorosiloxanes were observed using DMSO as the source of oxygen even though they were stable to the GC conditions. As linear α,β-dichlorosiloxanes are commercially available they were injected onto the GC and it was observed that no reaction or rearrangement occurred. They were, however, observed when iodosobenzene was used as the oxygen donor (see Section 2.7).

Brook also suggested that high concentrations of DMSO and times longer than 75 minutes were needed to observe a complete conversion of the dichlorosilane. In contrast we observed a complete conversion of Me_2SiCl_2 when low DMSO/ Me_2SiCl_2 concentrations were used, however, this did take up to four hours, albeit starting at -30 °C.

Despite the different conditions used to carry out this reaction, in both cases the conclusions were the same. Figure 2.4 compares the data obtained in our laboratory (a) and by Brook (b)



(a) Starting temperature: -30° (b) Starting at room temperature

Figure 2.4 – A comparison of the data obtained in our laboratory a) and by Brook.

Graph (b) was obtained by Brook using diethyl ether as the solvent and, following the reaction by ^{1}H-NMR. In Brook's graph compounds 1, 2 and 3 are the α,ω-disiloxane, trisiloxane, and tetrasiloxane respectively, D_3, D_4 as well as the starting material are also reported. Graph (a) shows the data obtained in our laboratory where the reaction was carried out in chloroform. It is clear, in both cases, there is a rapid decrease of Me_2SiCl_2 followed by a rapid increase of D_3 which then decreases in concentration in favour of the formation of larger rings. However, the main difference between the two sets of data is the presence of the α,ω-siloxane which we did not detect by GC when DMSO or the other oxygen donors were used, except in the case of iodosobenzene.

2.7 – Choosing different oxygen donors.

DMSO contains a nucleophilic oxygen attached to a potentially electrophilic heteroatom. This suggests that other compounds having similar characteristics may be used for cyclic siloxane formation, for example:

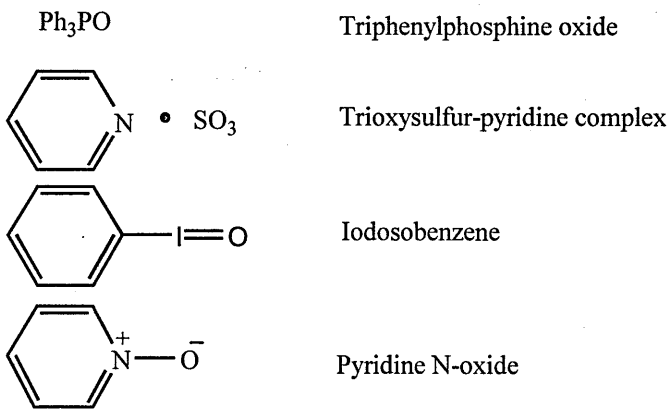
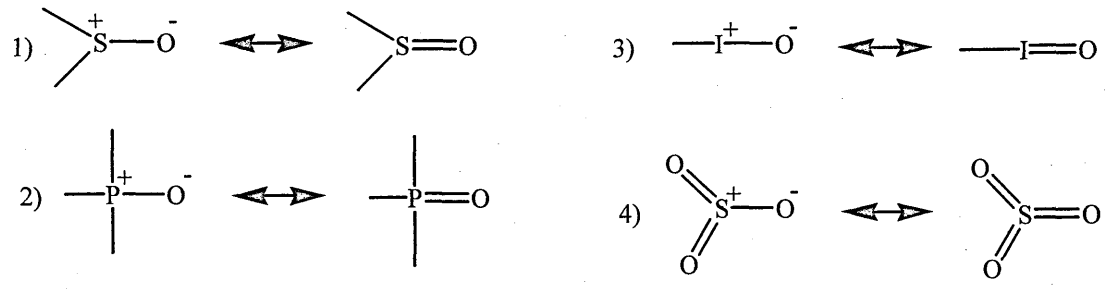


Figure 2.5 – Structures of the oxygen donors.

DMSO is generally used as a solvent because of its capacity to dissolve a large number of inorganic salts as well as the majority of organic compounds. Since sulphur can expand its electronic octet, it forms stable tri- and tetravalent compounds such as DMSO. In such compounds the sulphur is present in its high oxidation state and this makes the molecule a good source of oxygen in the condensation reaction.

A similar argument can be applied to the other compounds in Figure 2.5, that can be used as oxygen donors. All but the last compound can be represented by two resonance forms, one with a nucleophilic O^- and the other with the heteroatom oxygen in a high oxidation state, as shown in Scheme 2.9

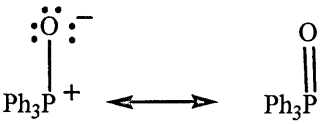


Scheme 2.9 – Resonance forms of the oxygen donors.

These compounds were all reacted with Me_2SiCl_2 at room temperature. As with DMSO, the reactions were monitored using GC and quantitative calculations made using an internal standard.

2.7.1 – Me_2SiCl_2 + Ph_3PO.

Triphenylphosphine oxide is the product obtained in the Wittig reaction where an aldehyde or a ketone is transformed into an alkene using a phosphonium ylide. The latter is a molecule that, when written in a Lewis structure showing all atoms with complete shells, has a positive and a negative charge on adjacent atoms. The intermediate in the Wittig reaction is an oxaphosphetane, an unstable four membered ring that rearranges into the phosphine oxide. The driving force of this reaction is the formation of the strong phosphorus-oxygen bond, which is stabilised by resonance:

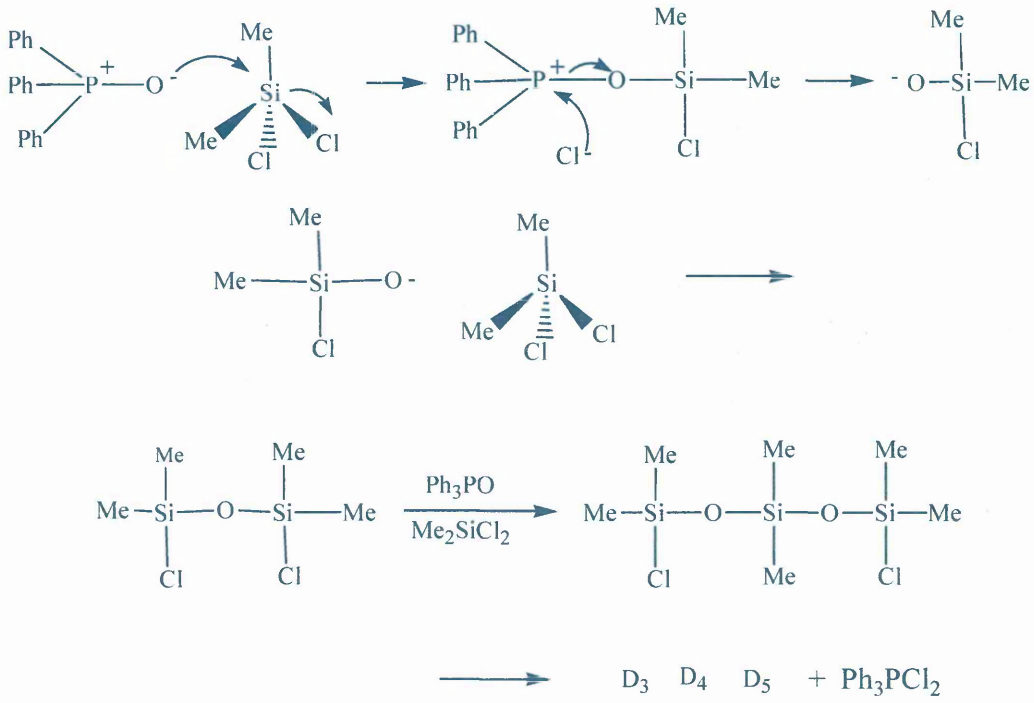


Scheme 2.10 – Resonance form in triphenylphosphine oxide.

The internal standard used for this reaction was biphenyl and Figure 2.7, on pages 62 shows the graph obtained by plotting the amount of D_3, D_4 and D_5, as well as dimethyldichlorosilane, versus time.

As with the DMSO reaction there is a very quick decrease in the concentration of the starting material. Again there is an initial increase in the amount of D_3 followed by a decrease, however the amount of D_3 does not decrease so dramatically, such that the amounts of D_4 and D_5 seem to be constant. In this case we believe the reaction has run out of oxygen donor compound.

As the reagent has the same characteristics as DMSO, it is reasonable to suggest that these reactions follow a similar mechanism to that proposed for DMSO, as shown in Scheme 2.11.



Scheme 2.11 – Proposed mechanism of rings formation.

The sudden decrease in the concentration of dimethyldichlorosilane could again be attributed to hydrolysis by fortuitous water. However, the ^{31}P-NMR of the reaction mixture using Ph_3PO after 5 min shows a change in chemical shift as Ph_3PCl_2 is produced; this confirms that the decrease of dimethyldichlorosilane is due to a non-hydrolytic process.

Figure 2.6 shows a comparison of the peaks for Ph_3PO, with a chemical shift of δ=31.2 ppm and Ph_3PCl_2 which has a chemical shift of δ=35.9 ppm. Both NMRs were recorded using H_3PO_4 as reference.

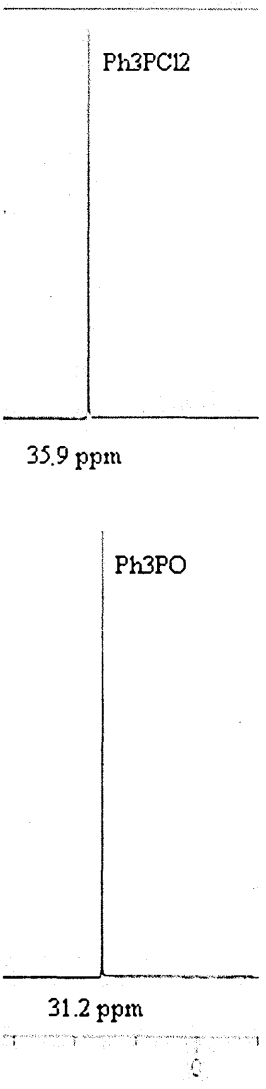


Figure 2.6 – Chemical shift of $Ph_3\ PCl_2$ and Ph_3PO in ^{31}P-NMR.

Amount of material/mmol				
Time (h)	Starting Mat.	D_3	D_4	D_5
0	9.41	0	0	0
0.03	3.11	1.82	0.74	0.21
0.05	2.41	1.60	0.76	0.18
0.5	2.94	1.99	0.86	0.18
1	3.07	2.46	0.96	0.19
1.5	3.15	1.92	0.86	0.18
2		2.06	0.81	0.15
5.5		1.74	0.95	0.25

Table 2.4 - Variation of the amounts of products and starting material with time for the reaction of Me_2SiCl_2 with Ph_3PO.

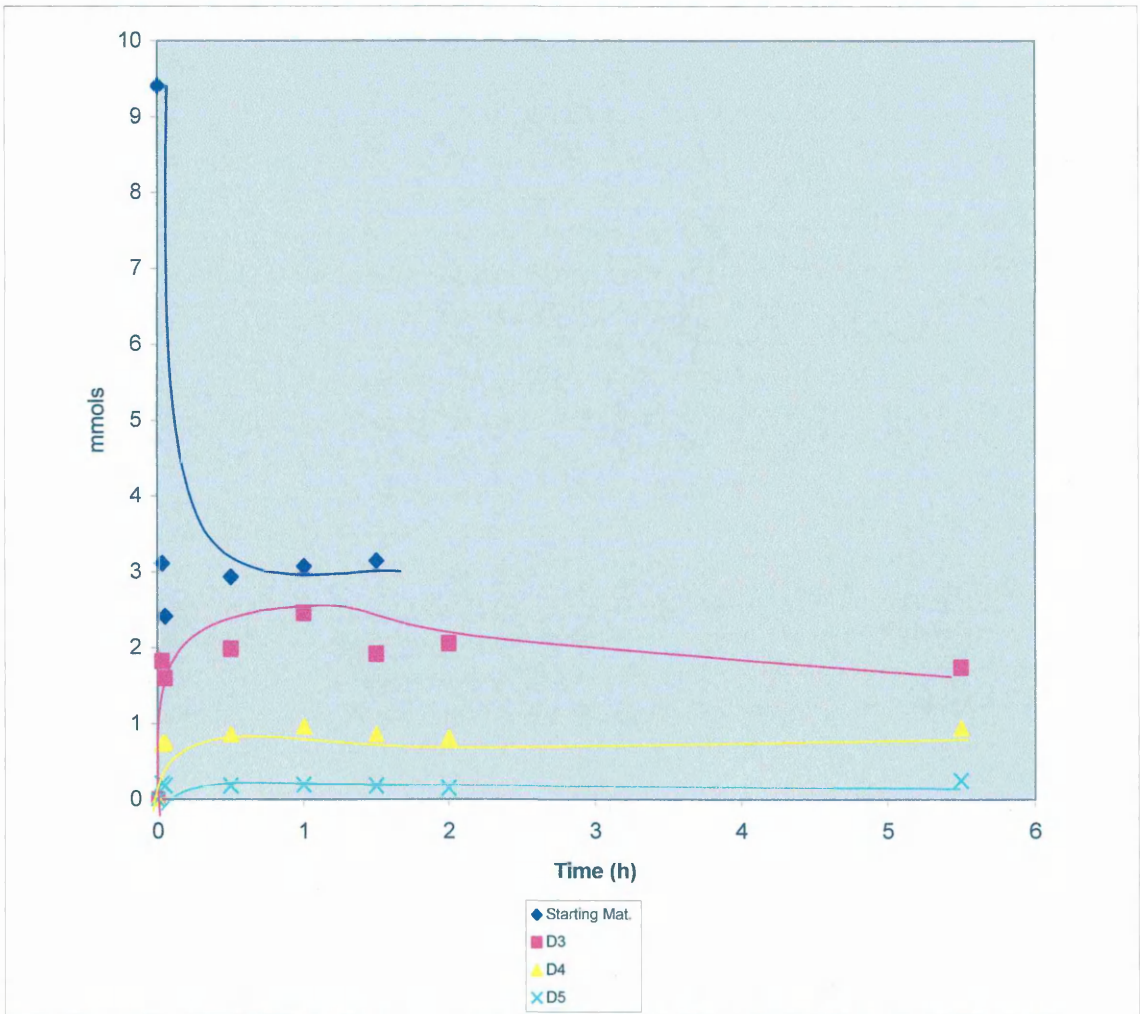


Figure 2.7 – Reaction products for Ph_3PO + Me_2SiCl_2 vs. time.

2.7.2 - Me_2SiCl_2 + Iodosobenzene.

Iodosobenzene was also chosen as a source of oxygen. Iodosobenzene is not commercially available and therefore it was necessary to prepare it. The synthesis consists of the chlorination of iodobenzene in chloroform using gaseous chlorine. The crystalline iodosobenzene was filtered and treated with sodium carbonate and then washed with water to remove the unreacted iodobenzene.

The reaction of iodosobenzene and dimethyldichlorosilane was performed under the same conditions as for the other oxygen donors: the dichlorosilane/oxygen donor ratio was maintained at 1:1 and chloroform was used as the solvent.

Figure 2.9 on page 64 shows the pattern for this reaction. With iodosobenzene, the reaction proceeds faster than with the other oxygen donors. The concentration of the starting material, dimethyldichlorosilane, decreases to zero in the first five minutes of reaction. In this instance we observed an increase in the amount of larger rings (greater than D_6), due to the subsequent rearrangement of D_3 and D_4 which decrease correspondingly. The rearrangement was shown to be promoted by the presence of the oxygen donor compound. The enlargement in the figure highlights the early stages of the reaction showing that the reaction went to completion after less than one hour.

Although the reaction is much faster than the others, it was possible to observe that the pattern of the graph is similar to that displayed by the others except that the amount of D_4 is almost 20 times more than that of D_3 even after a few seconds, although it decreased rapidly after five minutes of reaction.

Time (min.)	Starting Mat.	D_3	D_4	D_5
0	2.25	0	0	0
0.03	0.28	0.18	1.92	0.13
5	0	0.35	0.37	0.17
10		0.19	0.20	0.14
15		0.12	0.16	0.15
20		0.18	0.16	0.11
25		0.19	0.19	0.17
35		0.16	0.15	0.13
50		0.14	0.17	0.15

Table 2.5 - Variation of the amounts of products and starting material with time for the reaction of Me_2SiCl_2 with iodosobenzene.

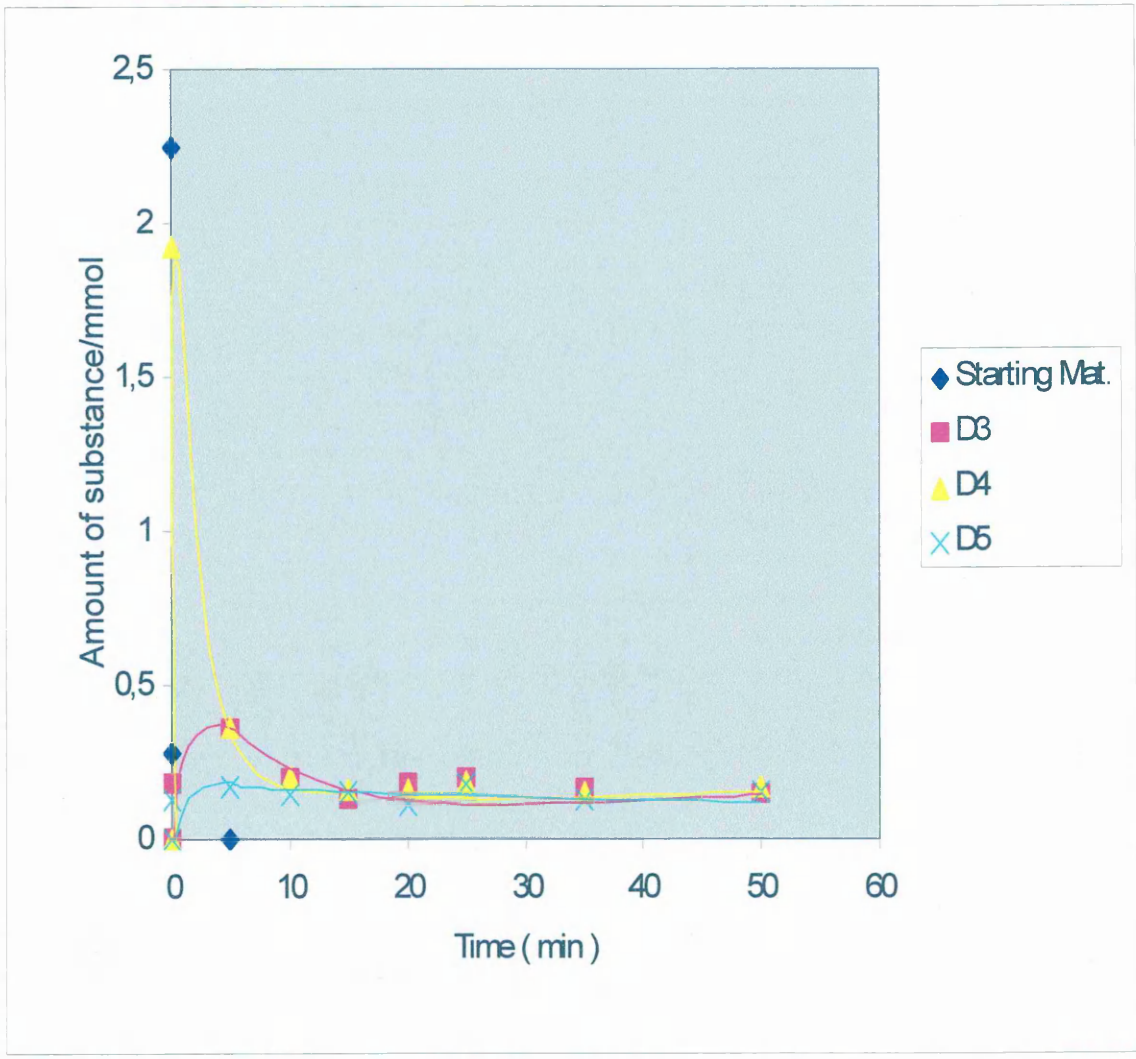


Figure 2.9 – Reaction products for Iodosobenzene + Me_2SiCl_2 vs. time.

The reaction with DMSO was exothermic and, in order to analyse the pathway of the reaction, it was necessary to cool the mixture. Despite the fact that no increase in

temperature was observed when the iodosobenzene solution in chloroform was added to the solution of the dichlorosilane, the reaction was so fast that it was not possible to observe the variation of D_3 in the very early stages of the reaction and cooling down the reaction mixture did not make a difference.

This system provides further confirmation of the mechanism proposed for this type of reaction. According to this mechanism, when iodosobenzene is the oxygen donor, the other reaction product is iodobenzenedichloride which is a particularly reactive chlorinating agent for aromatic systems such as the biphenyl which was used as the internal standard. The GC of the reaction mixture, using biphenyl as a standard, shows some peaks with retention times greater than biphenyl (12.82 min), at 15.91 min and 18.16 min GC/MS showed that these peaks could be attributed to *ortho* and *para* chlorobiphenyl respectively. Thus, it was necessary to change the standard to adamantane for this reaction.

As will be discussed in Section 2.10, a further experiment, to confirm the presence of a halogenating agent in the reaction with iodosobenzene, was carried out using anisole and either dimethyldichlorosilane or dimethyldibromosilane in the presence of iodosobenzene in carbon tetrachloride. GC/MS showed the presence of 2-chloroanisole and 4-chloroanisole and the corresponding bromo compounds.

The same experiment was repeated using other oxygen donor compounds (triphenylphosphine oxide, pyridine N-oxide and trioxysulfur pyridine complex); however, for these compounds no chlorination or bromination of anisole was observed (see Section 2.10).

2.7.3 - Me_2SiCl_2 + Trioxysulfur Pyridine complex.

The graph illustrating the reaction with the trioxysulfurpyridine complex, is similar to the Ph_3PO graph. However, in this case, as well as an initial burst, we observed a more gradual decrease in the concentration of dimethyldichlorosilane.

	Amount of material			
Time (h)	Starting Mat.	D_3	D_4	D_5
0	9.29	0	0	0
0.03	4.01	0.65	0.36	0.11
1	2.53	1.20	1.50	0.47
1.5	2.78	1.57	1.43	0.67
2	1.51	1.70		0.57

Table 2.6 - Variation of the amounts of products and starting material with time for the reaction of Me_2SiCl_2 with trioxysulfur pyridine complex.

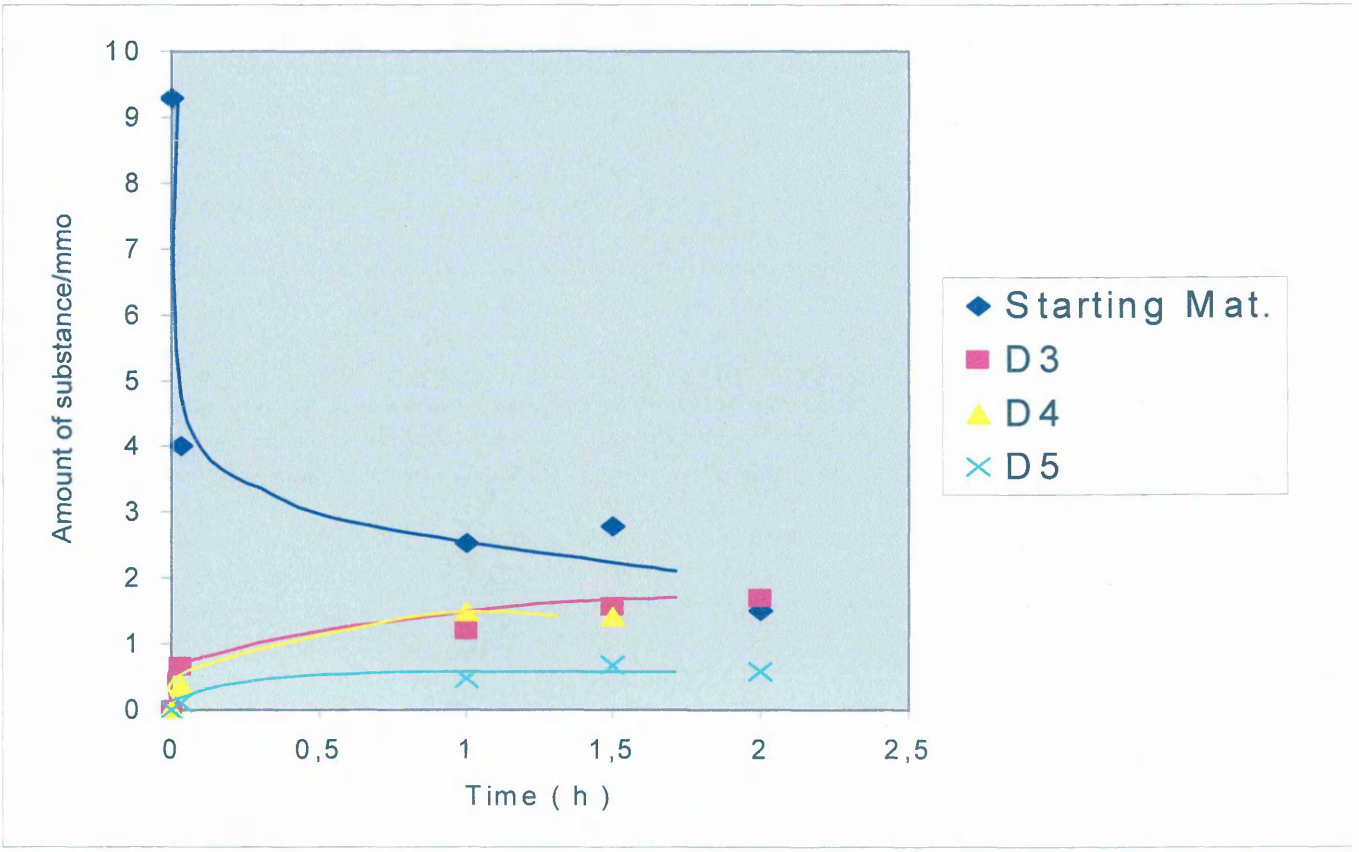


Figure 2.10 – Reaction products for trioxysulfur pyridine complex + Me_2SiCl_2 vs. time.

2.7.4 – Me_2SiCl_2 + Pyridine N-oxide.

The reaction with pyridine N-oxide was carried out using the same conditions as for DMSO. When the solution with the oxygen donor was added to the solution with the dichlorosilane a white precipitate was formed almost immediately. The reaction was monitored by GC as for the other reaction and the white solid was analysed separately.

The first analysis of the white solid was to test its solubility. As the white solid was not soluble in chloroform, after filtration it was tested in non-polar solvents such as diethyl ether as well as very polar solvents such as methanol and water. Methanol turned out to be the best solvent and this allowed us to record the NMR spectrum of this precipitate. ^{29}Si-NMR did not show any peaks but the ^{1}H-NMR was quite revealing. Our first thoughts were that the white solid was pyridine N-hydroxide which could be formed due to the presence of acid/water in the mixture. The ^{1}H-NMR, recorded using TMS as a reference, showed two sets of triplets with chemical shifts of 8.1 ppm and 8.4 ppm respectively and a doublet at 8.9 ppm. These peaks were attributed to the pyridine ring. A sharp singlet with a chemical shift of 5.1 ppm was initially attributed to the OH group of the pyridine N-hydroxide. The spectrum also showed a very small peak at δ = 3.3 ppm arising from the methanol. A second proton NMR, was recorded after adding more methanol to the initial solution. This should have increased both the peaks at δ = 3.3 ppm and δ = 5.1 ppm. However, only the peak at δ = 3.3 ppm increased, with no change to the peak at δ = 5.1 ppm, suggesting the peak did not arise from an –OH group.

The absence of a peak for the OH group made us think that the solid formed might be pyridine N-chloride, the expected chlorinated product as was formed with DMSO. Additional evidence for this comes from the amount of solid obtained (overall 0.5 g) as well as the IR analysis, which did not show the characteristic broad peak in the region of 3.300 cm^{-1} arising from the hydroxy group. Further characterisation of this product was not

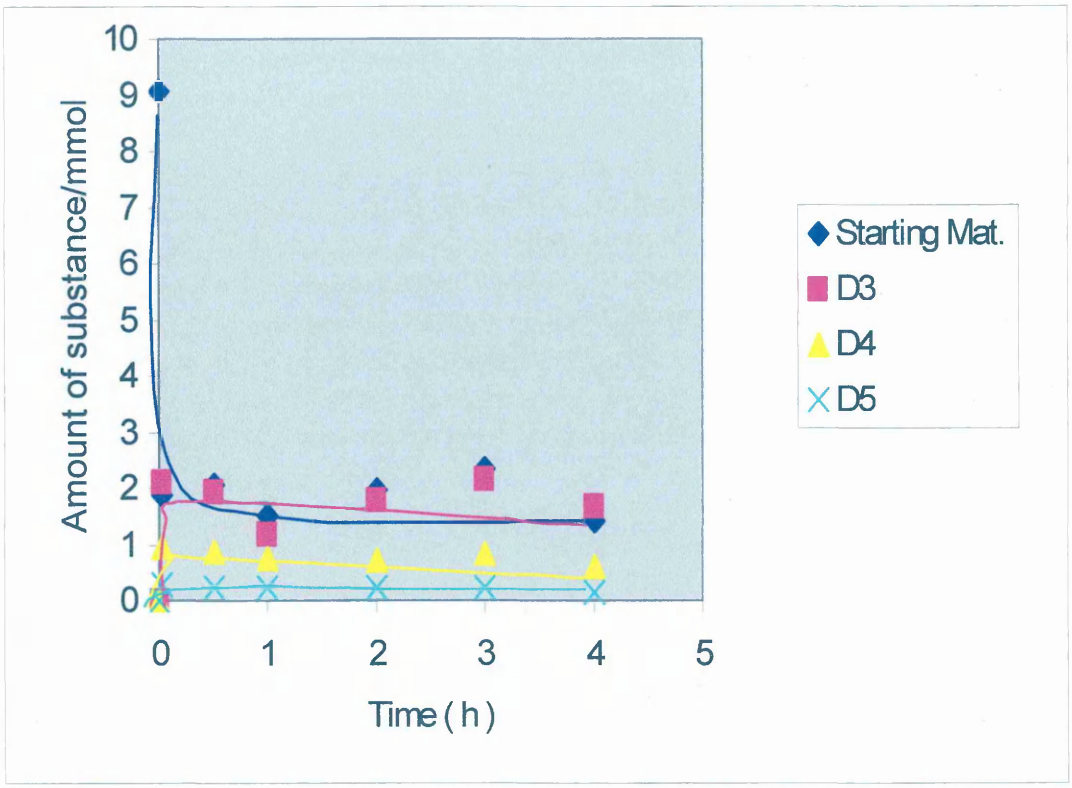
possible because the solid was a powder and therefore no single crystal X-ray diffraction could be carried out. Mass spectrometry was not as helpful as expected: the major fragmentation occurred at the N—X bond and therefore, only a peak at m/z 79 was observed confirming the presence of the pyridine ring.

Figure 2.7 shows how the concentrations of products varied with time. Once the D rings were formed, pyridine N-oxide did not show any exchange, $D_3 \rightarrow D_4 \rightarrow D_5$. The concentration of the starting material Me_2SiCl_2 did not end up at zero but the reaction seemed to stop. This is probably because the oxygen donor was completely consumed and therefore the dichlorosilane runs out of reagent.

	Amount of material			
Time (h)	Starting Mat.	D_3	D_4	D_5
0	9.06	0	0	0
0.03	1.88	2.10	0.95	0.28
0.5	2.07	1.95	0.87	0.24
1	1.51	1.17	0.75	0.22
2	1.96	1.80	0.72	0.24
3	2.35	2.16	0.84	0.24
4	1.41	1.69	0.60	0.15

Table 2.7 - Variation of the amounts of products and starting material with time for the reaction of Me_2SiCl_2 with pyridine-N-oxide.

Figure 2.7 – Reaction products for Pyridine N-oxide + Me_2SiCl_2 vs. time.

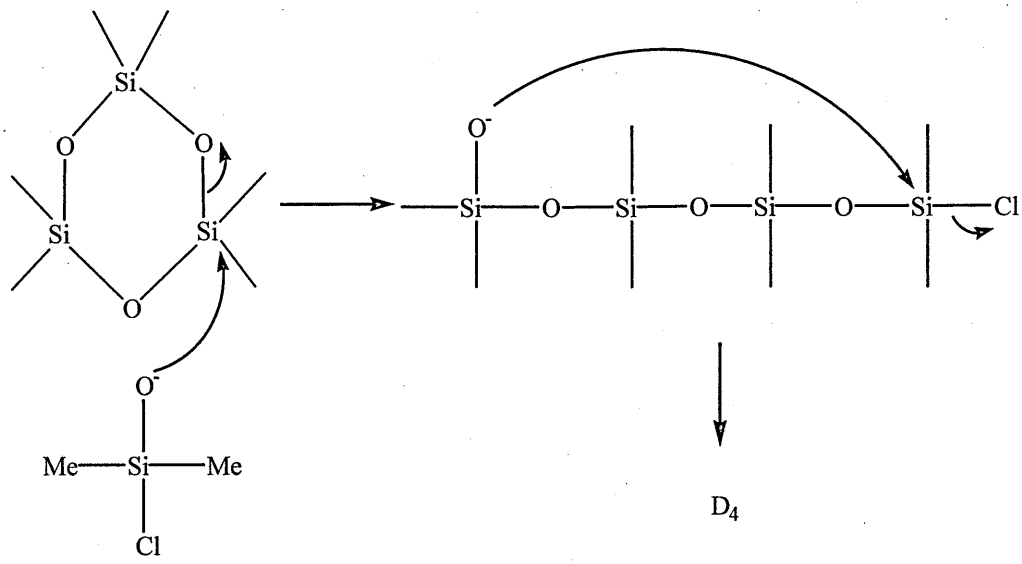


2.8 – Conversion of D_3 into larger rings.

As mentioned earlier, D_3 is formed as a major product in the early stages of the reaction. Figure 2.1 clearly shows that D_3 is subsequently converted into D_4 and D_4 presumably converted into D_5 and subsequently into larger rings. D_3 is therefore the kinetic product when this "hydrolysis" is carried out in the absence of water.

The mechanism of formation of D_3 (and D_4 and D_5) assumes the formation of an intermediate α,ω-dichlorosiloxane. Cyclisation of the appropriate α,ω-dichlorosiloxane thus initially gives D_3 with some D_4, D_5 etc.

The ring strain energy, as well as the planar shape of the ring, makes the D_3 molecule susceptible to nucleophilic attack and ring opening.



Scheme 2.12 – Proposed mechanism of rearrangement of D_3 into larger rings.

So it is not unexpected that once formed, the D_3 ring opens and rearranges into larger and more thermodynamically stable rings such as D_4 and subsequently D_5. The intermediacy of the D_3 ring in D_4 and D_5 ring formation was confirmed by the observation that a pure sample of D_3 underwent ring opening under the conditions of the experiment (see Section 2.13).

2.9 – Optimisation of the yield using different ratios of the oxygen donor to the dichlorosilane (1:1.5).

We thought we may be able to increase the yield of D_3 or at least aid its isolation by increasing the concentration of the dichlorosilane in the reaction mixture. For this reason an oxygen donor/dimethyldichlorosilane ratio of 1:1.5 was used. Figure 2.8 and Table 2.8 in the following page display the result of this study:

Amount of material			
Time (h)	D_3	D_4	D_5
0	2,08	1,82	0,75
1	1,94	2,01	0,68
1,5	1,98	2,54	1,02
2	1,48	3,32	1,23
2,5	0,55	2,11	0,86
3	0,43	2,13	0,78
4	0,44	2,38	0,81
5	0,42	2,47	0,87

Table 2.8 - Variation in the amount of larger rings obtained by rearrangement of D_3.

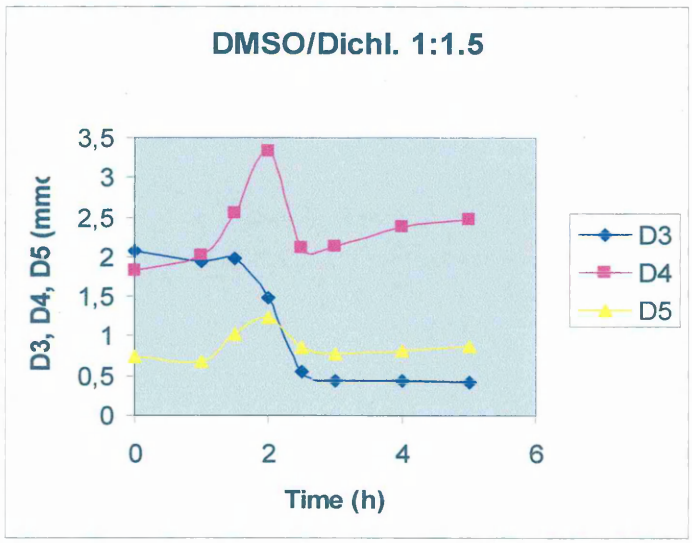
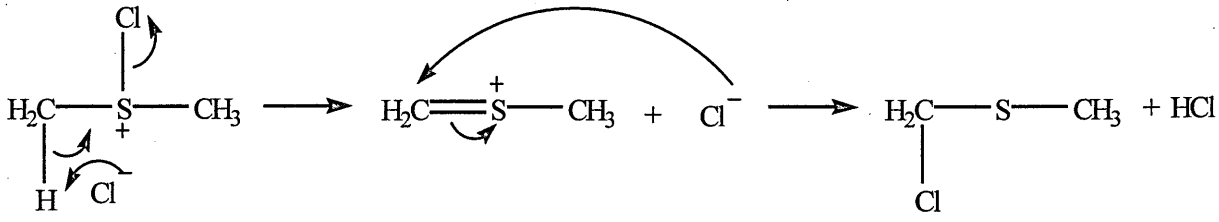


Figure 2.8 - Pattern of the conversion of D_3 into larger rings.

The graph, as expected, displays a similar pattern to that reported previously. The only observable change is that the reaction proceeds faster, but no change in the relative proportions of D_3, D_4 and D_5 was observed, suggesting that changing the ratio of reactants would not aid the isolation of D_3. Figure 2.3 showed an increase then decrease in the concentration of D_3 and an accompanying increase in the amounts of D_4 and D_5. Figure 2.8 reveals more of the reaction sequence with D_4 and D_5 showing a similar increase then decrease, presumably at the expense of larger rings. Eventually the concentrations level off as all the DMSO is consumed.

2.10 – Chlorination of anisole.

As discussed earlier, biphenyl was not suitable as an internal standard for the reaction involving Me_2SiCl_2 and iodosobenzene. This was because of the further reaction of the iodosobenzenedichloride product. We reported earlier that, in the case of DMSO, the corresponding by-product is the chlorodimethylsulfonium chloride, **2.13** which undergoes a further rearrangement according to the following scheme:



2.13 **2.14**

Scheme 2.13

Whilst product **2.13** in Scheme 2.13 cannot be detected on the GC, product **2.14** is detected with an early retention time. In the case of iodosobenzene the corresponding chloro compound is iodobenzenedichloride, shown in Figure 2.9.

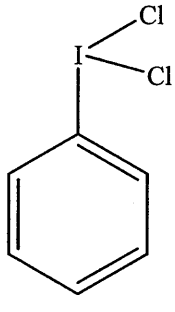


Figure 2.9 – Structure of iodobenzenedichloride

Such a chloro compound is a particularly reactive chlorinating agent and it reacts with the biphenyl standard to give the 1-chloro-2-phenylbenzene, as confirmed by GC/MS. This

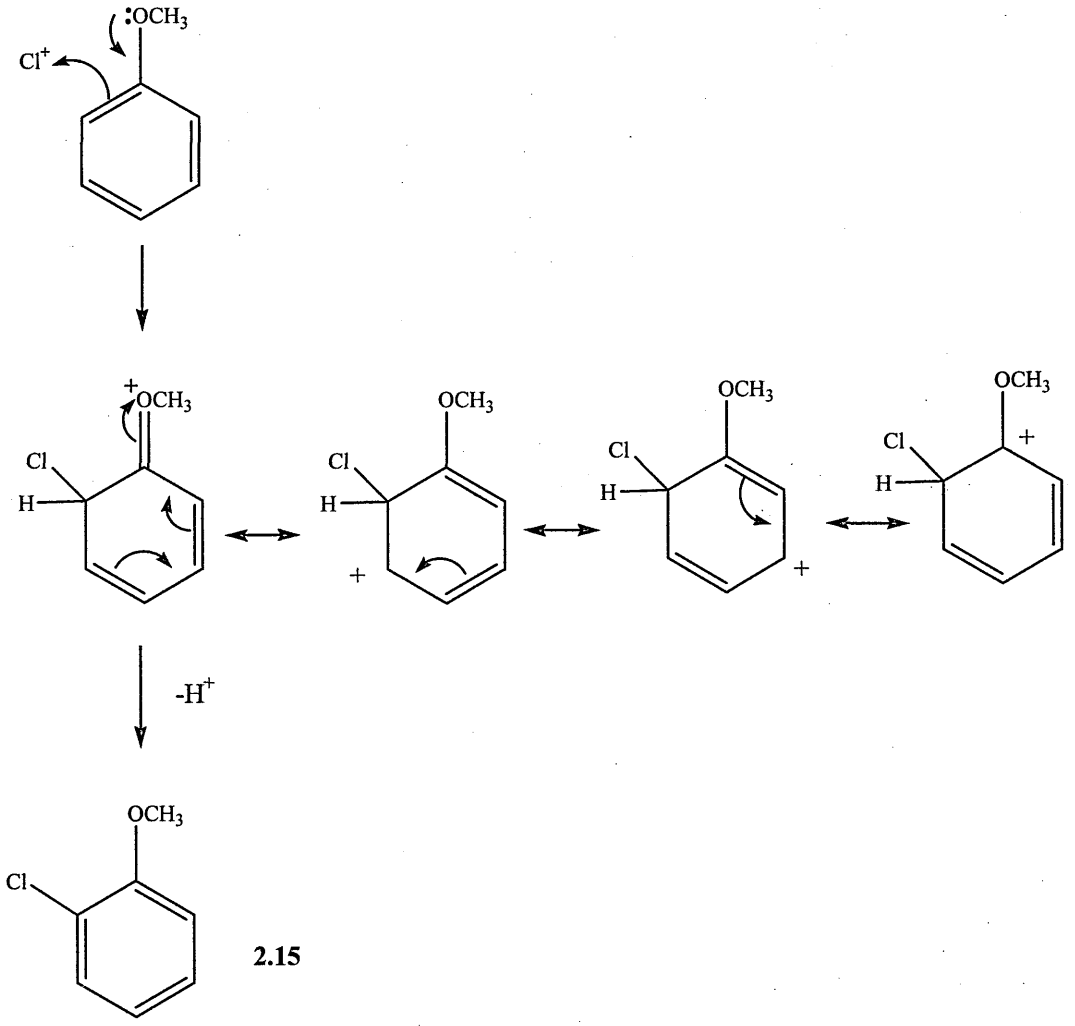
halogenation product was detected only when iodosobenzene was used as the source of oxygen. The other oxygen donor compounds probably rearranged to less electrophilic species, as with DMSO, but the final compounds obtained were not detected with the analytical methods we used. Furthermore, since no chlorination was observed this suggests that the rearrangement occurred before the reactive chlorine compound could halogenate the ring.

This result was very interesting and we therefore performed a more detailed investigation. Anisole, a reactive aromatic compound like biphenyl, was reacted in a non-aqueous and non-acidic medium with a chlorosilane (Me_2SiCl_2) or bromosilane (Me_2SiBr_2) in the presence of an oxgen donor compound. Anisole contains a benzene ring and an electron donating group. This would lead to mainly *ortho* and *para* substituted products.

The reaction was carried out with a range of oxygen donor compounds, in carbon tetrachloride and the mixture stirred over a period of 24. During this time the reaction was followed by GC every four hours, quenching the mixture in sodium bicarbonate in order to neutralize the HCl formed during the reaction. The formation of the expected products was confirmed by comparison with commercial 2-chloroanisole, 3-chloroanisole and 4-chloroanisole. Injections of the three different chloroanisoles onto the GC gave retention times of 17.00 min, 17.88 min and 17.54 min for the 3-chloroanisole, 2-chloroanisole and 3-chloroanisole, respectively.

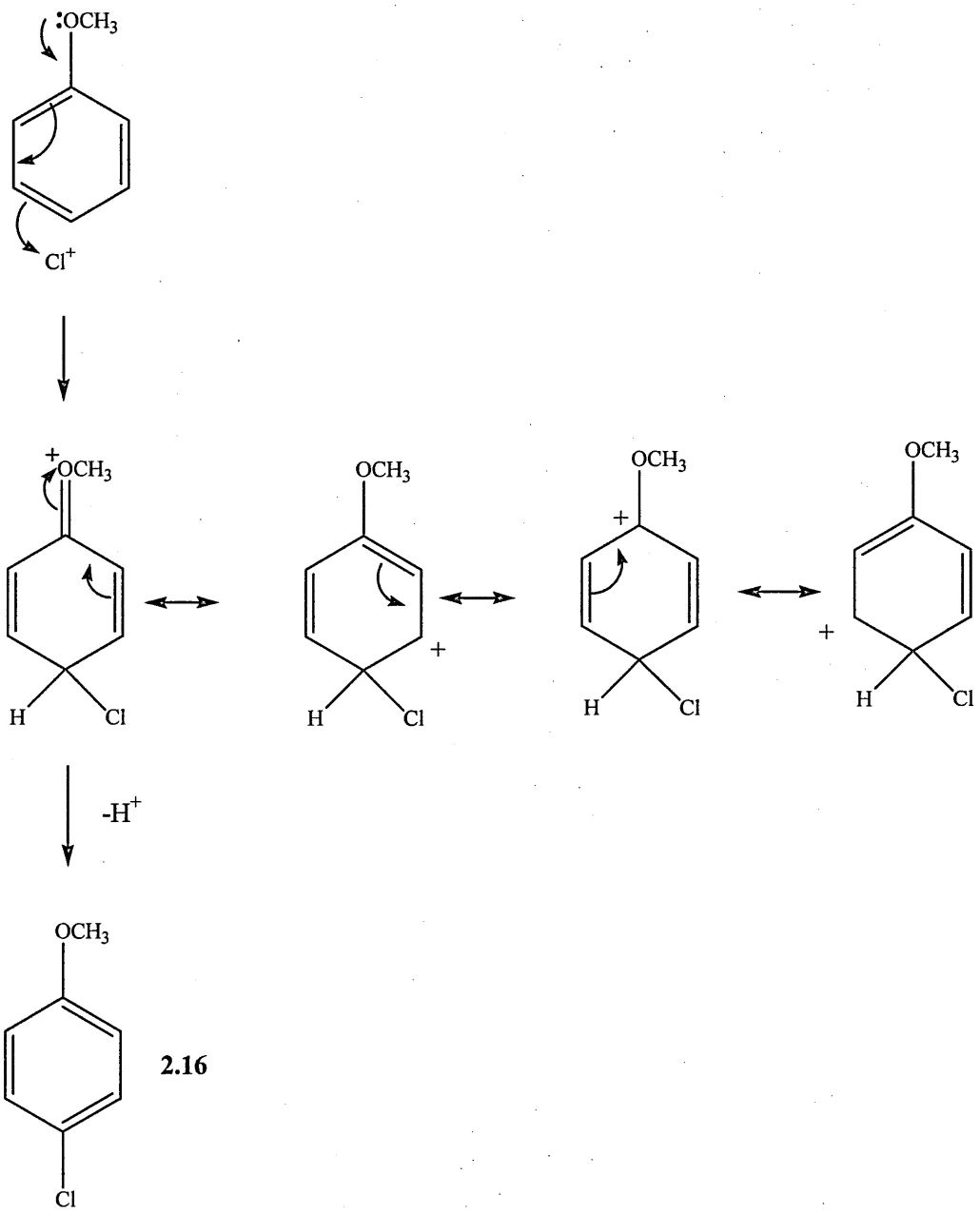
As expected, only one peak, that of the starting material, anisole, was observed when the reaction with Me_2SiCl_2 or Me_2SiBr_2 was performed in the presence of pyridine-N-oxide, triphenylphosphine oxide, trioxysulfur-pyridine complex and DMSO as the source of oxygen. When iodosobenzene was used, the peaks corresponding to the 2-chloro (**2.15**) and 4-chloroanisole (**2.16**) were present with no trace of the 3-chloroanisole. The result is

compatible with the directing effect of the methoxy group which orients the attacking Cl^+ towards the *ortho* and *para* position.



2.15

a)



2.16

b)

Scheme 2.14 – Mechanism of the chlorination of anisole in a) *ortho* and b) in *para* position

A phenyl ring attached to the benzene ring has a similar effect to an $-OCH_3$ group and therefore an aromatic substitution, such as chlorination, occurs predominantly *ortho* and *para* to the phenyl substituent. Thus, when biphenyl was used as the standard, three products, other than D_3, D_4 and D_5, were observed during the reaction. GC/MS analysis of

the major two products gave the same molecular weight of 188 (+190 ratio 3:1) but with different retention times. Following the results obtained with the anisole it is reasonable to assume that the two products obtained were the 2- and 4-chloro-1-phenylbenzene. The third minor product gave a mass spectrum with peaks at 222, 224 and 226 (in a ratio of 9:6:1) corresponding to an isomer of the dichlorobiphenyl.

The chlorination of the anisole and biphenyl only occur because of the formation of the iodobenzenedichloride. The compound was available, because it was an intermediate in the synthesis of the iodosobenzene, thus a pure sample of iodobenzenedichloride was reacted with the biphenyl using chloroform as the solvent. The GC/MS analysis confirmed the presence of the *ortho* and *para* chlorobiphenyl. Two more peaks with retention times of 9.8 min and 10.23 min respectively were also present in the reaction mixture which were attributed to the 1-chloro-2-iodobenzene and 1-chloro-4-iodobenzene respectively. The reason why these two compounds were not observed in the reaction with Me_2SiCl_2 is still not clear.

A similar study using dimethyldibromosilane gave the corresponding *ortho* and *para* bromoanisoles. Thus, the reaction of iodosobenzene with halosilanes not only provides a route to D ring species but a means of halogenating aromatic compounds in organic media in the absence of acids.

2.11 – Using different solvents other than $CHCl_3$ in the "Non-aqueous hydrolysis" reaction.

The best yields of D_3 in all the experiments described previously were obtained using DMSO as the oxygen donor compound with choloroform as the solvent.

Part of the aim of this work was to improve the yield of D_3 and one way of optimising the yields was to use different solvents. Thus, the reaction using DMSO as the oxygen donor compound was carried out in different solvents such as water and heptane (although we might expect the aqueous hydrolysis to compete with the DMSO reaction). These two solvents were chosen because of their polarity: choloroform has a polarity intermediate between water (a very polar solvent) and heptane (a non polar solvent). The ratio of dichlorosilane/DMSO used was again 1:1 and the total volume of solvent was maintained the same.

The reaction in water generated a two phase mixture when the DMSO was added to it. After three hours stirring, the organic products were extracted into CH_2Cl_2 since, due to the column used in the GC, the reaction mixture in water could not be injected directly. The solvent was reduced in volume by rotary evaporation and then injected onto the GC. No relevant peaks were observed corresponding to the retention times of D_3, D_4 or D_5. The presence of the water probably hydrolysed the dichlorosilane to give the corresponding disilanol. However no ring formation was observed either from the reaction with water or with DMSO.

The addition of the DMSO to the reaction mixture usually generates an increase in the temperature. In order to avoid the evaporation of a volatile solvent, the reaction with heptane required an ice bath to reduce the temperature to 0 °C. The temperature was kept low during the addition of the dichlorosilane, and the mixture was stirred until it reached room temperature.

A white solid was observed in the solution during the addition of the DMSO but injection onto the GC of this solid at room temperature confirmed that it was frozen DMSO. However, after warming to room temperature, injection of the crude mixture onto the GC revealed the start of the reaction with the formation of the D rings. Since the use of hexane

did not lead to large improvements in the yield of D_3 with respect to the other rings we decided that chloroform seemed to be the best solvent to perform such reactions.

2.12 - Oxygen donors + Me_2SiCl_2 test runs followed by ^{29}Si-NMR.

In this project we reacted the dimethyldichlorosilane with a range of compounds which acted as a source of oxygen and followed the reaction by gas-chromatography. When this project started in late 1997 Brook's paper was not yet been published (it was published in May 1998).

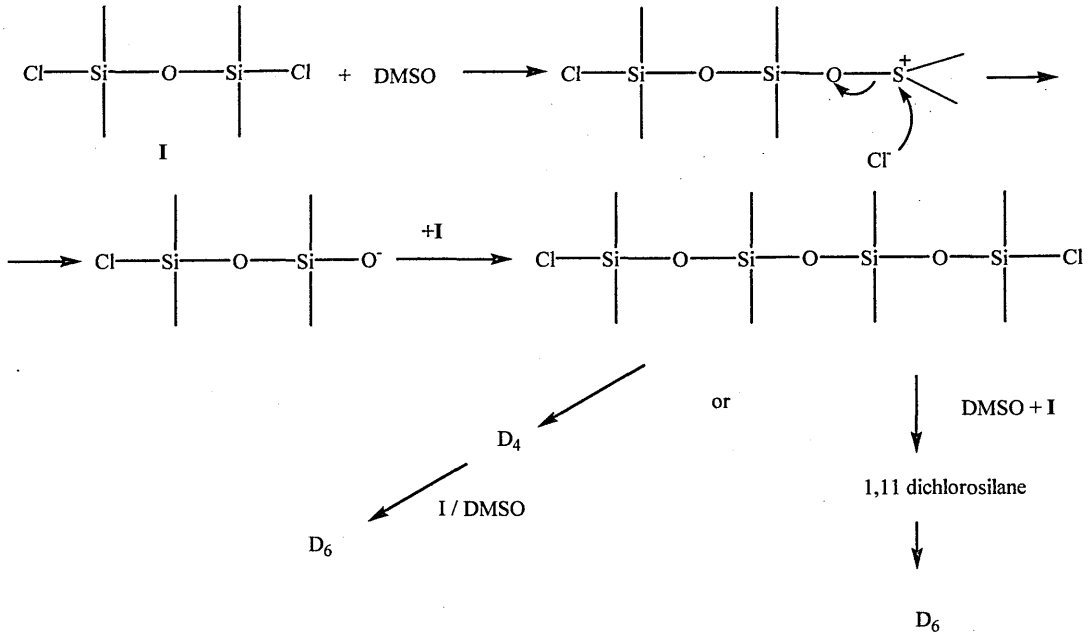
A comparison of our results and Brook's results, which were related only to DMSO, show the same pattern (Section 2.6). Brook monitored the reaction by ^{29}Si-NMR and so, in order to confirm that we achieved the same observations, we also monitored the reaction by ^{29}Si-NMR.

The reaction was performed in an NMR tube using deuterated chloroform as solvent. The ratio of chlorosilane to oxygen donor was the same as that used in the tests previously described (1:1), and the spectra were recorded every five minutes.

As the purpose of this set of reactions was to confirm that the same results were obtained using GC and NMR, we did not use an internal standard to analyse the reaction products quantitatively. However, the variations in the intensity of the peaks confirmed that the concentration of D_3 increased in the early stage of the reaction and then decreased in favour of the formation of larger rings and in particular D_4 and D_5.

In the proton NMR we also observed the formation of 1,3-, 1,5- and 1,7-dichlorosiloxanes, especially in the early stages of the reaction, which are then converted into rings by an intramolecular nucleophilic attack.

Furthermore, when DMSO was added to a solution of pure 1,3-dichlorodisiloxane in $CDCl_3$, we observed only D_4 and D_6 and larger rings. This is a powerful confirmation that ring formation does not go via an intermediate silanone but via α,ω-dichlorosiloxanes as shown in Scheme 2.16.



Scheme 2.16

The presence of only even numbered siloxane units confirms that the reaction goes via the proposed mechanism involving α,ω-dichlorosiloxanes and not silanones that would lead to D_3 and D_5 compounds as well.

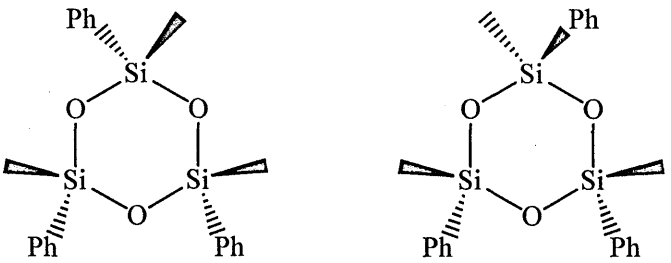
2.13 - "Non-aqueous" hydrolysis with addition of D_3.

The conversion of D_3 into larger rings is thought to be due to ring opening and addition of siloxane units onto the linear D_3 species. This is only possible when the dichlorosilane is still present in solution. In order to confirm this mechanism of conversion of D_3 into larger rings, a pure sample of D_3 was reacted with the oxygen donor compounds in chloroform as

solvent. Analysis of the reaction mixture by GC and ^{29}Si-NMR with the time showed that no change in the amount of D_3 occurred and, as a consequence, there was no formation of D_4 and D_5 or any other larger rings. However, when the dichlorosilane was added to the reaction mixture, we obtained the same pattern as observed in the earlier reactions, that is a decrease in the amount of D_3 (below it's original concentration) as a consequence of the formation of D_4, D_5 and larger rings.

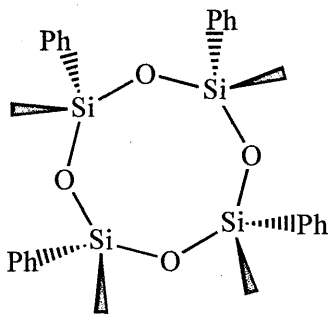
2.14 - Disubstituted chlorosilanes.

The planarity of the Si_3O_3 ring was observed in 1950 by Aggarwal and Bauer[12] based on an electron diffraction study of hexamethylcyclotrisiloxane. As a result consequently of this planarity, dimethylsubstituted D_3 does not display any form of isomerism. However, isomerism is encountered with methylphenylcyclosiloxanes. Ordinary hydrolysis of methylphenyldichlorosilane gives two cyclotrisiloxane ring isomers and four cyclotetrasiloxane ring isomers. Figures 2.10 and 2.11 show the possible isomers for $^{Ph}D_3$ and $^{Ph}D_4$. All of these isomers have been synthesised separately and appropriate data is available in the literature.



2.17 **2.18**

Figure 2.10 – Isomers of $^{Ph}D_3$.



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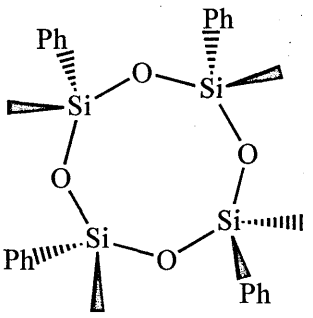

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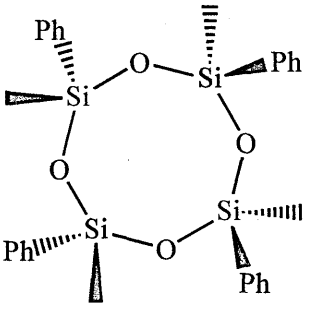

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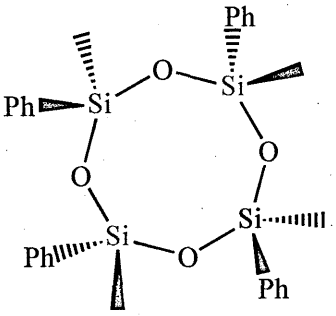


2.22

Figure 2.11- Isomers of $^{Ph}D_4$.

The silicons marked in different colours in Figures 2.10 and 2.11 represent different chemical environments in the ^{29}Si-NMR and therefore it is reasonable to expect several peaks in the NMR spectrum according to the number of chemical environments. In the case of a D_3 ring, three peaks are expected in the D_3 region due to the presence of two isomers. A mixture of isomers of a disubstituted tetrasiloxane is, in fact, even more complicated giving 6 peaks. In such cases it is difficult to attribute each peak to the corresponding isomer.

Table 2.3 lists the ^{29}Si NMR chemical shifts we obtained for $^{Ph}D_n$ and $^{H}D_n$:

$^{X}D_n$	Chemical Shift
$^{Ph}D_3$	-20.82
	-20.95
$^{Ph}D_4$	-30.74
	-30.81
	-30.94
	-30.10
$^{Ph}D_5$	-33.08
	-33.88
$^{H}D_3$	
$^{H}D_4$	-31.96
	-32.05
	-32.25
	-32.33
	-32.57
	-32.64
$^{H}D_5$	-34.73
	-34.80

Table 2.3 – Chemical Shifts of disubstituted D_n rings.

It is interesting to observe that the presence of a phenyl group moves the chemical shift by about 10 ppm when compared to the dimethyl analogues because of its sp^2 hybridisation.

To investigate the proportion of these stereoisomers formed by non-hydrolytic means, $PhMeSiCl_2$ was reacted with DMSO. The conditions in which these reactions were performed were the same as previously described: the ratio of DMSO:dichlorosilane was 1:1 and the solvent used was chloroform. After 24 h, the reaction mixture was analysed by GC and ^{29}Si-NMR. The ^{29}Si-NMR of the crude reaction mixture is shown in Figure 2.12 and contains peaks in the D_3, D_4 and D_5 regions. As discussed in Chapter 1, the ^{29}Si-NMR peak areas can sometimes be used quantitatively (within reason) to attribute a peak to a particular silicon atom, however, such an analysis requires the sample to give well resolved NMR signals. Unfortunately analysis of a reaction mixture containing many rings, as well as the presence of other compounds, made assignment of the peaks very difficult.

The gas chromatogram is shown in Figure 2.13, and contains two peaks.

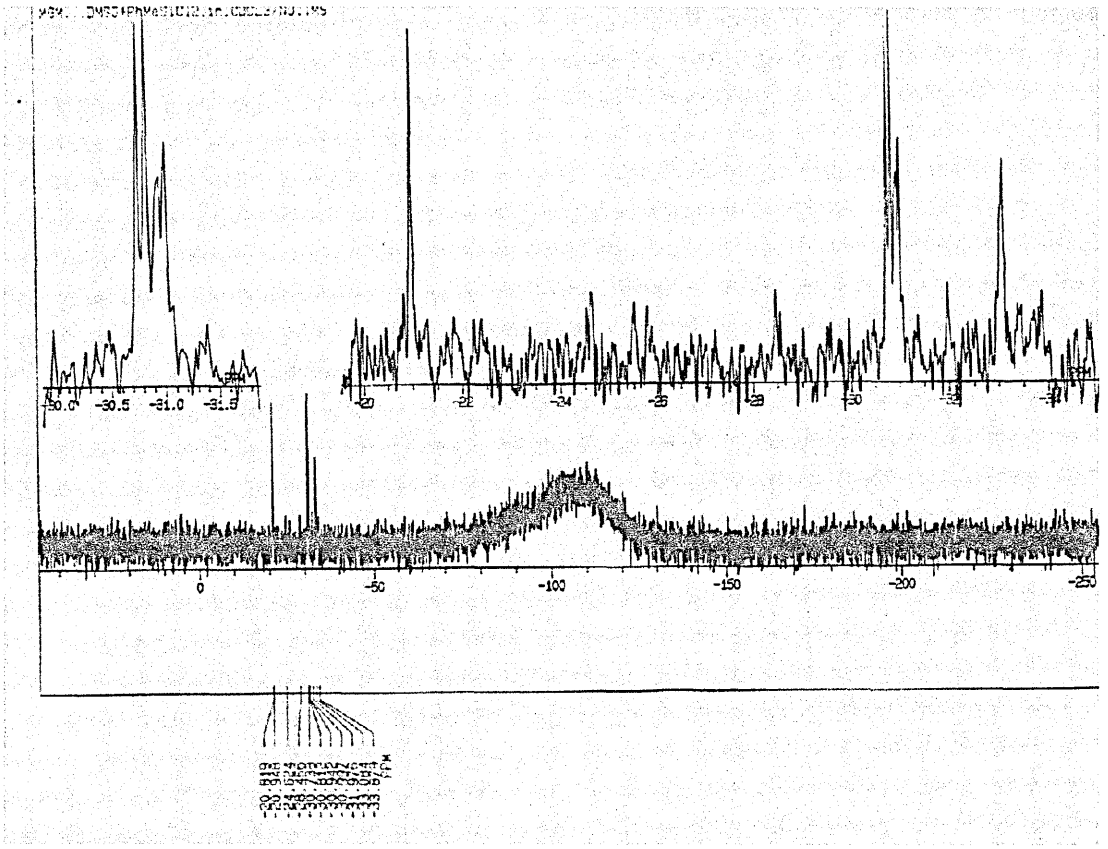


Figure 2.12 – ^{29}Si-NMR of the reaction with $PhMeSiCl_2$+DMSO.

with retention times of 14.49 min and 15.74 min respectively and a group of four peaks with retention times of 23.74 min, 26.58 min, 27.30 min and 28.25 min.

As each isomer has a different arrangement of atoms in space, it is reasonable to expect that each isomer will have a different retention time. Thus, we can attribute the first two peaks in the GC to the two isomers for $^{Ph}D_3$ and the subsequent four peaks to isomers of $^{Ph}D_4$.

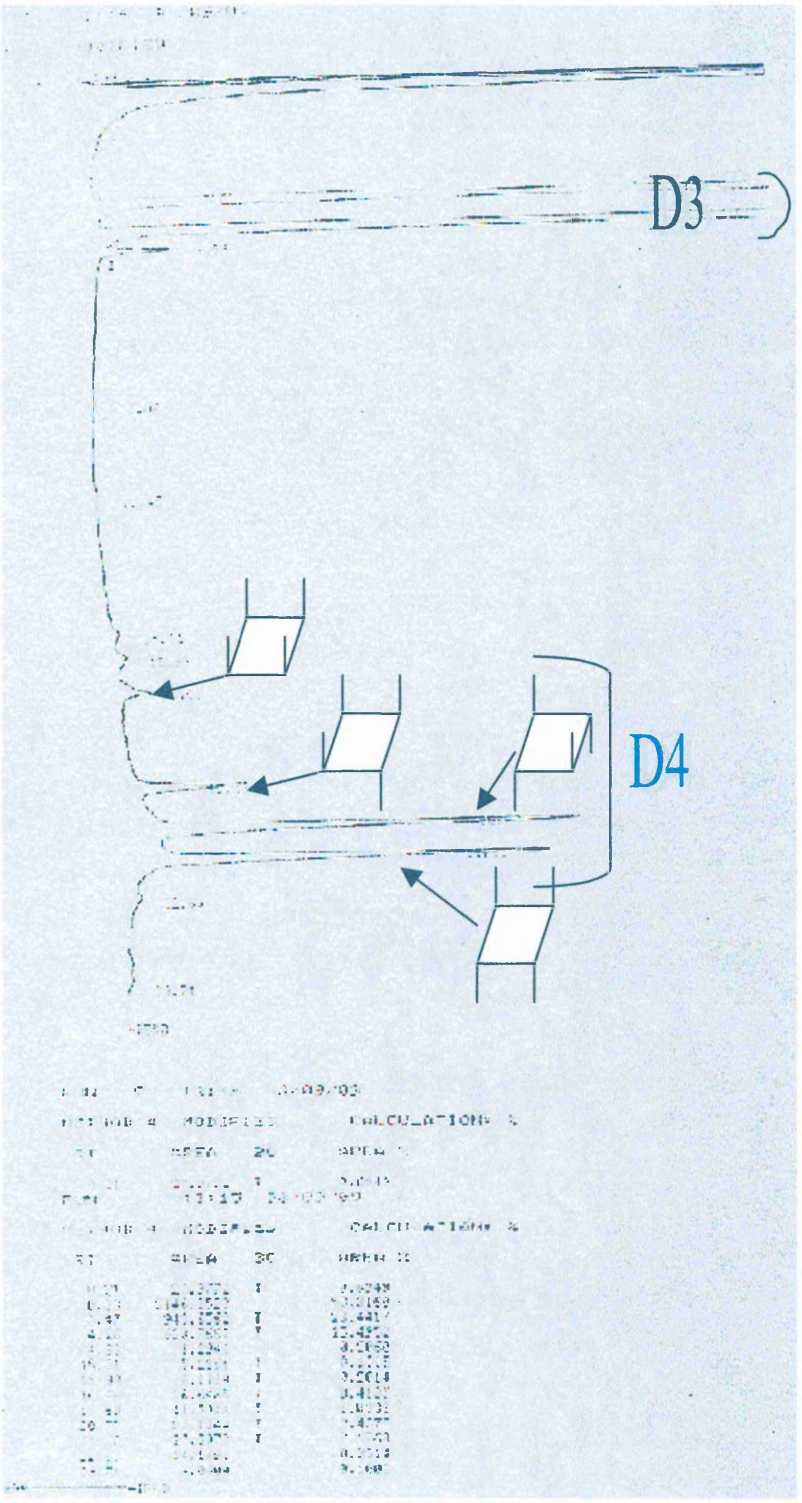
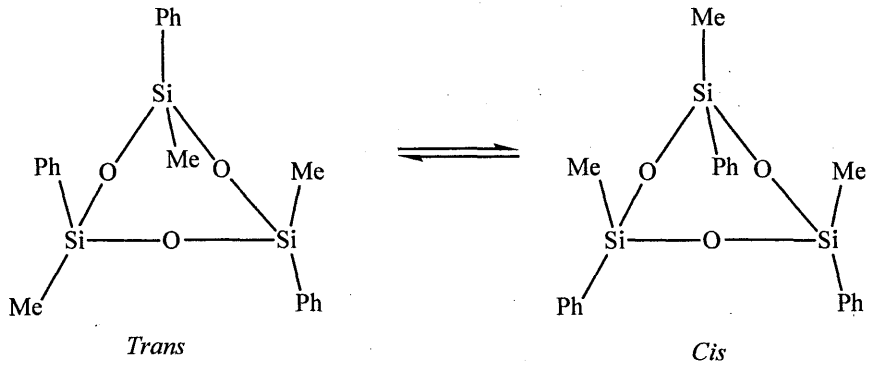


Figure 2.13 – Gas chromatogram of the mixture of isomers of $^{Ph}D_3$ and $^{Ph}D_4$.

Scheme 2.16 shows the equilibrium between the *cis* and the *trans* forms:



Scheme 2.16 – Equilibrium of the *cis* and *trans* isomers.

Alvarez[197] has shown that at room temperature this equilibrium consists of 52% of the *trans* and 48% of the *cis* isomer. Table 2.3 on page 82 shows that, according to the peak areas, an equilibrium mixture of the *cis* and the *trans* isomers is obtained; that is, there is no preference for either of the two forms.

According to the literature a mixture of isomers is not observed in the hydrolysis of methyl**hydro**dichlorosilane although we might expect the same set of isomers to be obtained as with $PhMeSiCl_2$. To confirm this result using non-aqueous hydrolysis, $MeHSiCl_2$ was reacted with DMSO. As with the previous reaction, it was monitored by GC. After 3.5 hour, the chromatogram contained three peaks with retention times: 3.04 min, 5.37 min and 7.61 min.

2.15 – Conclusion.

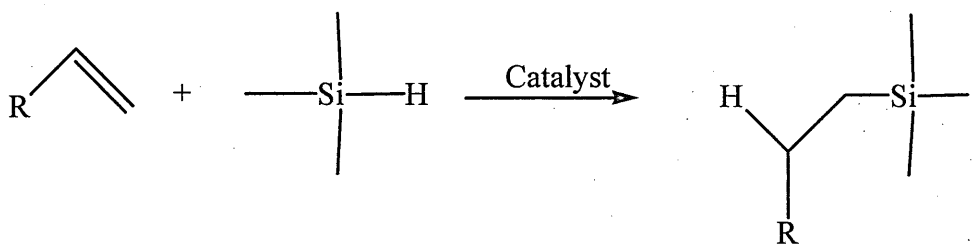
The synthesis of Dx rings has been explored in this chapter using different compounds as a source of oxygen to form the Si—O—Si bond. The different potential sources of oxygen used were: DMSO, pyridine N-oxide, iodosobenzene, trioxysulfurpyridine complex and triphenylphosphine oxide.

The main target was to optimise a method which led preferentially to D_3. This target could be achieved successfully by optimising the reaction conditions and varying the source of oxygen.

We demonstrated that DMSO, compared to the other oxygen donor compounds, gave the maximum amount of D_3 relative to the other D rings obtained in the reaction mixture. Nevetherless conversion of D_3 into larger ring cannot be completely excluded regardless of the oxygen donor used due to the large ring strain in D_3. The six membered ring, as in D_3, has a planar shape making ring strain energy more evident. The planarity of the molecule, due to the larger O—Si—O angle also makes the silicon atom in the siloxane bond more easily attacked by a nucleophilic group thereby opening the ring.

This explains the interconversion of the D_3 ring into the thermodynamically more stable larger rings that have lower ring strain.

DMSO was also reacted with methylhydrogendichlorosilane. The product ($^{H}D_3$ which, as described for D_3, also reacts to form larger rings) has an Si—H bond which offers good opportunities for further investgations. The hydrogen, in fact, can be substituted, via hydrosilylation (see chapter 3 for more details about such reaction) with other functionalities in accordance with the following scheme 2.17:



Scheme 2.17 – General reaction of hydrosilylation

providing a reagent offering chances for further investigations. R could be any kind of group also carrying other functionalities including a linear chain of hydrocarbon with another double bond at the end in order to generate linear and/or cross linked polymers

where the hydrocarbon chain separates the D_3 rings giving ideas for further investigations into the chemistry of silicone polymers.

CHAPTER 3

"NON-AQUEOUS" HYDROLYSIS OF TRICHLOROSILANES: SYNTHESIS OF FUCTIONALISED T_6

3.1 – Silsesquioxane cages. A brief introduction.

Silsesquioxanes are three dimensional polyhedral silicon oligomers that can take the form of cages, partially or completely condensed ladders and also randomly distributed networks.

They have a general formula of $(RSiO_{1.5})_n$ where "n" is usually an even number and R is generally methyl, halogen, phenyl or simply hydrogen. They have received a great deal of attention, especially in the last few years, as cores for building octopus molecules[180] and dendrimers[181], as models of resins, and as starting materials for the preparation of partially opened cages that themselves act as models for silica surfaces and supports for transition metal catalysts[182].

Octasilsesquioxane cages have been known since 1965 and they represent one of the most fascinating classes of silsesquioxanes so far synthesised. Because of their structure, researchers refer to them as spherosiloxanes. In the early years they were regarded as curiosities since they seemed to have limited use and their synthesis was time-consuming. However, as a result of their specific molecular formulae and their controlled physical properties, the interest in such molecules has increased dramatically in recent years. Nevertheless, only a limited range of spherical organosilsesquioxanes have been prepared even though a large variety of trichlorosilanes are available[183].

In general, the synthesis of silsesquioxanes, involves the condensation of tri-functional monomers. A commonly used method is the complete hydrolytic condensation of monomers such as $HSiCl_3$.

3.2 – Synthesis of Silsesquioxanes: hydrolysis of trichlorosilanes.

As described in the introduction, there are mainly two methods used to synthesise spherical silsesquioxanes.

The mechanism of hydrolysis of trichlorosilanes in the presence of a limited amount of water has been already described: such scarce water syntheses involves the presence of an iron(III) salt ($FeCl_3$) where the iron probably acts as a templating agent for forming the cage. Furthermore, such syntheses can be performed in a mixture of different solvents, in order to control the equilibrium yields, based on the solubility of the different reagents and reaction products.

The formation of cages via such hydrolysis involves the formation of α-chloro-ω-hydroxysiloxanes and α,ω- dichlorosiloxanes; these oligomers can undergo a cross-linking rearrangement. In this way the linear siloxanes rearrange into two and three-dimensional molecules such as ladders and cages.

Silsesquioxane cages can also be prepared by conventional aqueous hydrolysis, as reported in 1965 by Brown[184]. According to Brown's paper, such reactions should lead to a mixture of different sized cages including T_6, T_8, T_{10} and T_{12}. The trichlorosilane used by Brown was phenyltrichlorosilane and the reaction was carried out in a mixture of acetone and water. Each silsesquioxane was separated from the others by recrystallisation from an alkaline solution of the phenyltrichlorosilane in different solvents.

Brown's procedure has been performed several times in our laboratory but the results were very different from those reported in his paper (these results will be discussed in Chapter 4: Linear and cyclic polyols).

The reactions described in the literature for the synthesis of T cages, including the "scarce water" hydrolysis, lead mainly to resin and a large variety of other products. Only when specific alkyl groups are present and/or solubility differences large enough is a particular cage favoured to such an extent, as to enable its isolation of pure silsesquioxane cages. Hydrogen octasilsesquioxane $H_8Si_8O_{12}$ can, in fact, be prepared by the "scarce water" method and can be easily isolated by crystallisation from hexane. Nevertheless, generally the yields obtained by such hydrolytic methods are poor and the octasilsesquioxanes, $(RSiO_{1.5})_8$, T_8, seem to be the usual outcome with a maximum yield of 4-5%.

An alternative route to functionalised T_8 species, is the formation of the spherical hydrogen silsesquioxane followed by hydrosilylation using alkene arms.[1] We have used this approach to build T_8 molecules with a range of functionalities, dendrimers, liquid crystals and surfactants.

Hydrosilylation is the most commonly used reaction for the formation of a Si-C bond and involves the addition of Si–H across a π bond. Normally the multiple bond is a C=C or a C≡C bond. In commercial terms, hydrosilylation is the most important technique for making Si-C bonds after the Direct Process. It is also one of the methods of choice in the laboratory since it permits the introduction of functionalized silanes (Si-Cl, Si-OR) or alkylsilanes into organic molecules in high yield. Hydrosilylation takes advantage of the relatively weak Si-H bond. The reaction may be initiated by radical or transition metal catalysis. In this thesis, transition metal catalysis will be described as it was the method of choice for the synthesis of trichlorosilanes with appropriate functionalities.

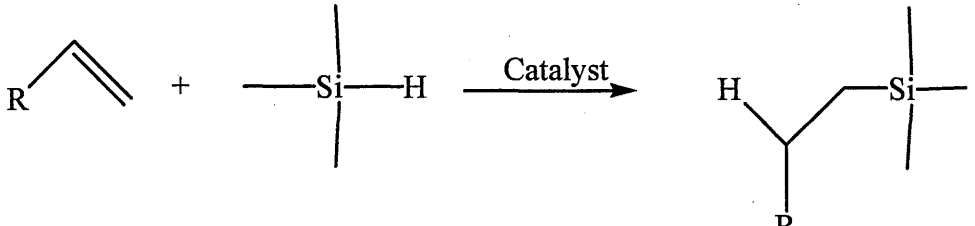
3.3 - Hydrosilylation with a platinum catalyst: mechanism.

Functionalised T_8 cages are commonly prepared via a two step method: the first step consists in the preparation of the octahydro-T_8. This is followed by the substitution of the hydrogen with an appropriate arm; this second step is generally performed via hydrosilylation[172].

We will see later in this thesis that this method is not applicable for the formation of functionalised T_6 because hydrogenated T_6 is not normally obtained by the method described and therefore the subsequent hydrosilylation cannot be performed.

Since hydrosilylation is a general method of substituting a hydrogen on a silicon with an organic functionality, starting from the trichlorosilane, $HSiCl_3$, it is possible to obtain a range of different trichlorosilanes which are not commercially available. In fact, although functionalised T_6 cages cannot be obtained via the hexahydro-T_6, in this thesis we used hydrosilylation to synthesise functionalised trichlorosilanes which were subsequently used to synthesise the corresponding T_6 via the DMSO procedure.

Silicon carrying a hydrogen atom is particularly susceptible to addition to a double bond according to the following general reaction scheme:



Scheme 3.1 – The hydrosilylation reaction.

Supported platinum catalysts have been known for some time to be poor catalysts for hydrosilylation. In the late 1950s Speier discovered that soluble chloroplatinic acid (H_2PtCl_6 in *iso*-propanol) was an efficient catalyst for such a reaction. The discovery permitted hydrosilylation to be used in commercial technology for the first time

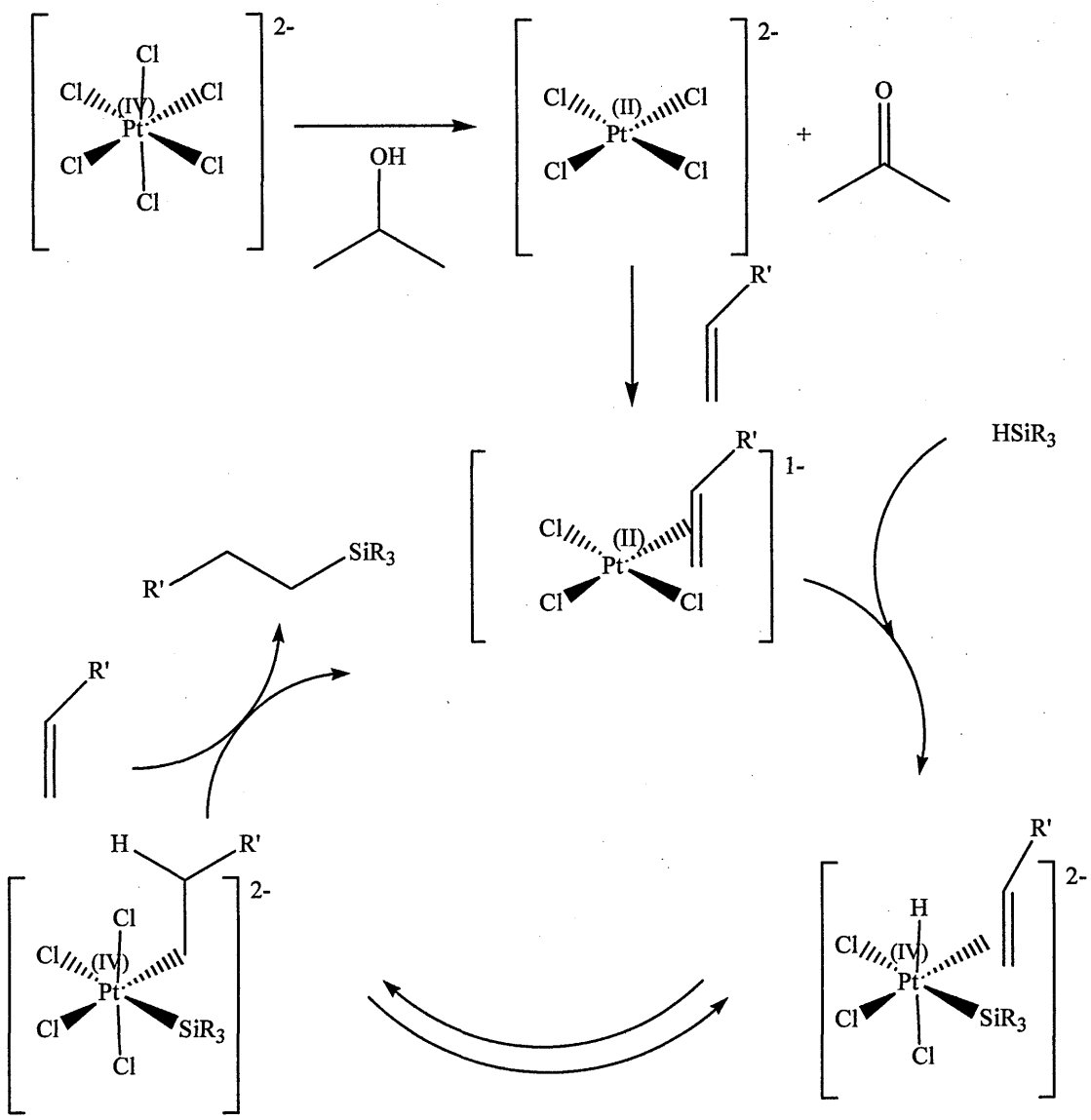
[173,174]. More recently, many other catalysts based on Pt^0 species (particularly Karstedt's catalyst[175] $Pt_n(H_2C{=}CH\ (CH_3)_2SiOSi(CH_3)_2CH{=}CH_2)_m$, n=2, m=3), have appeared. The relative rates of hydrosilylation depend on three parameters, the catalyst, the olefin and the hydrosilane[176]. The most commonly invoked mechanism for platinum catalysed hydrosilylation is that of Chalk and Harrod based on an analogy between the proposed reactive platinum catalyst species and isolated iridium complexes.[177, 178]

Several observations must be explained by the mechanism:

1. A concentration of 10^{-2} M catalyst is needed to catalyse the reaction under perfect conditions.
2. There is an induction period before the reaction itself takes place and, after such a period, the reaction is very fast.
3. It is known that reduction of the platinum takes place during the reaction.[179]

   $Pt^{IV} \rightarrow Pt^{II}$ (proposed active catalyst)[177] $\rightarrow Pt^0 \rightarrow$ Pt colloids

The mechanism of the hydrosilylation with a Pt catalyst is shown in Scheme 3.2. The solvent in which the catalyst is dissolved plays a key role in the reaction. The first step involves the reduction of the platinum from the oxidation state (IV) to the oxidation state (II) and in so doing the isopropyl alcohol is oxidised to the corresponding ketone.



Scheme 3.2 – A possible mechanism of action of the Pt catalyst.

3.4 – The aim of this work.

The aim of this part of the project was the preparation of functionalised hexasilsesquioxanes, T_6. Unfortunately, we have been unable to prepare hydrogen hexasilsesquioxane using any of the methods described above and thus cannot use

our hydrosilylation methodology. We therefore examined alternative methods of T_6 formation.

3.5 – Synthesis of R-T_6 - Previous work.

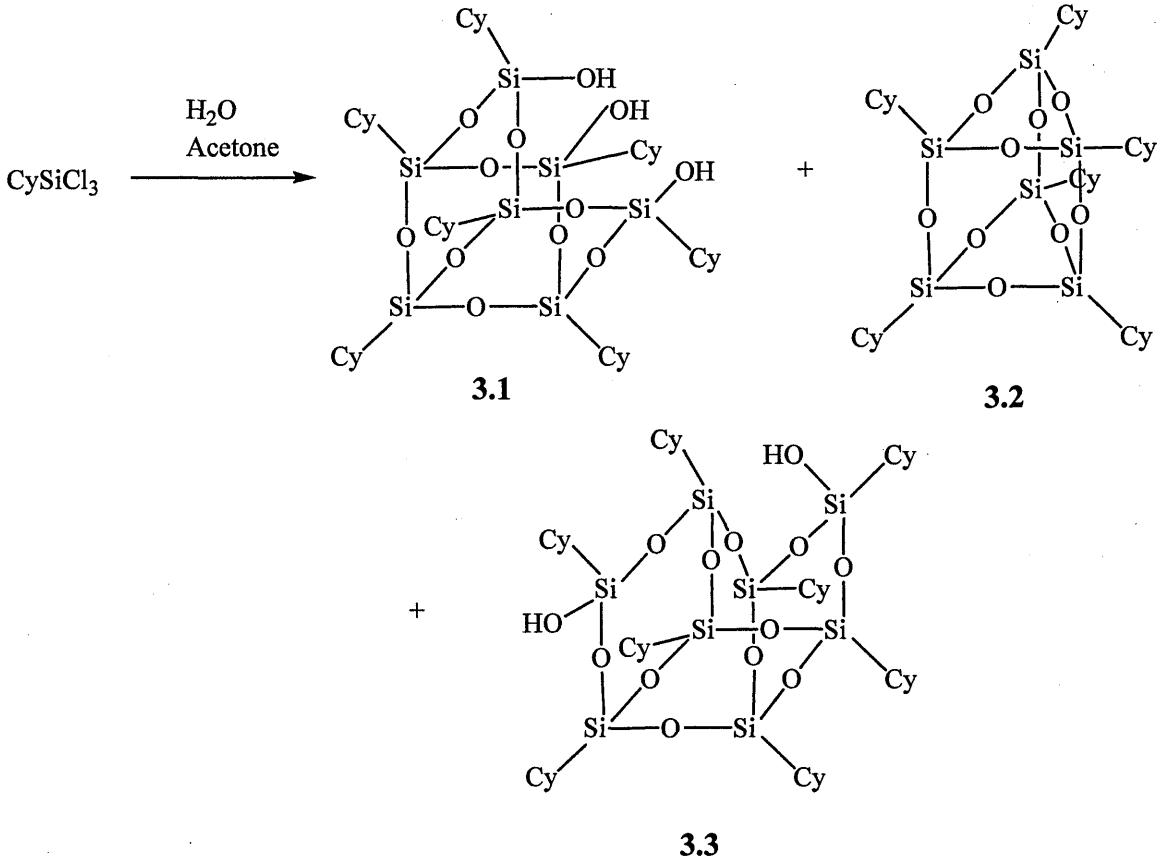
The first synthesis of R-T_6 is attributed to Brown and Vogt and was reported in 1965[184]. According to their procedure the hydrolysis of $PhSiCl_3$ in a mixture of water and acetone (with excess of water) leads, after a period between 3 to 35 months, to a mixture of a crystalline product and a resinous residue. In 1994 Molloy obtained sufficient crystals to carry out an X-Ray crystal structure analysis[185] of the crystalline product which corresponds to Cy-T_6 but it was obtained after four months of hydrolysis.

In 1998 the synthesis reported by Brown was rediscovered by Feher and co-workers. Hexa(cyclohexylsilsesquioxane) has been prepared by Feher[182] using the method of Brown[184], involving the aqueous hydrolysis of $CySiCl_3$ in a water/acetone mixture. The characterization of the products in the resinous mixture allowed Feher to write a general reaction scheme for the Brown procedure, as shown in Scheme 3.3. Some of

$$CySiCl_3 \xrightarrow[\text{Acetone}]{H_2O} \text{Linear siloxanes polymers + Partially condensed cages + Cages}$$

Scheme (reaction) 3.3 – General reaction leading to cages (Brown's procedure).

the reaction products in the resinous mixture are cages and partially condensed cages as shown in Scheme 3.4:



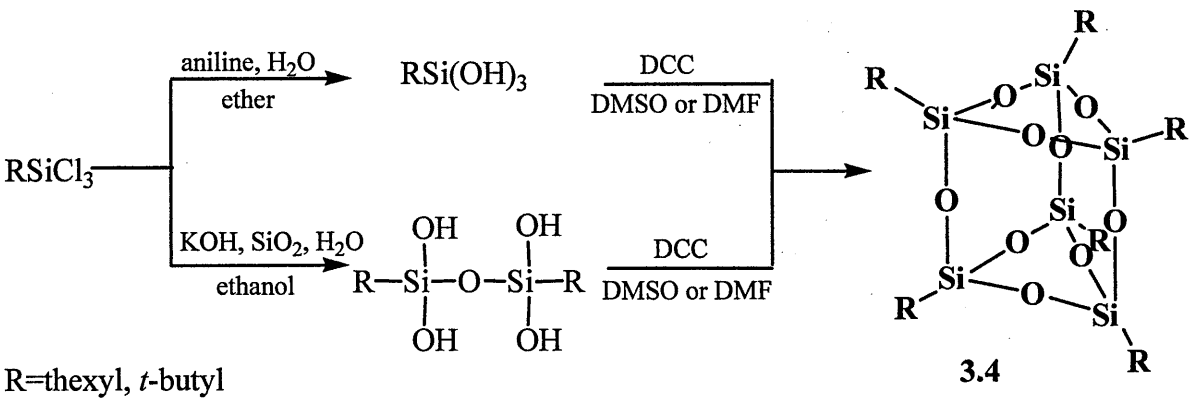
Scheme 3.4 – Cages and partially condensed cages obtained with Brown's procedure

Reasonable yields of these species are obtained, but only after long periods, usually months. The relative yields of the products obtained by Feher were respectively 45% for **3.1**, 40% for **3.2** and 15% for **3.3**. In this paper he also reported the characterisation of product **3.1** by X-ray diffraction. The X-ray diffraction crystal structure is also reported for compound **3.3** after derivatisation of the –OH groups with $SnPh_3$. Compound **3.2** was only characterised by ^{29}Si-NMR.

We have obtained reasonable yields of T_6 molecules in a shorter time using a similar aqueous/organic hydrolysis. We have used the conditions developed by Frye[203] and subsequently Feher, which involved the hydrolytic condensation of the corresponding trichlorosilane using concentrated hydrochloric acid in a mixture of methanol, toluene and hexane and using iron chloride as catalyst. However this route, similar to the synthesis of larger cages, is limited to a few compact substituents with

secondary or tertiary groups adjacent to the silicon, such as cyclohexyl and cyclopentyl groups.

Unno has developed an alternative approach to T_6 based on the dicyclohexylcarbodiimide coupling of the silane triol or 1,1,3,3-tetrahydroxydisiloxane.[186] Unfortunately this route to T_6 cages was only possible with bulky substituents such as *tert*-butyl and 1,1,2-trimethylpropyl groups.

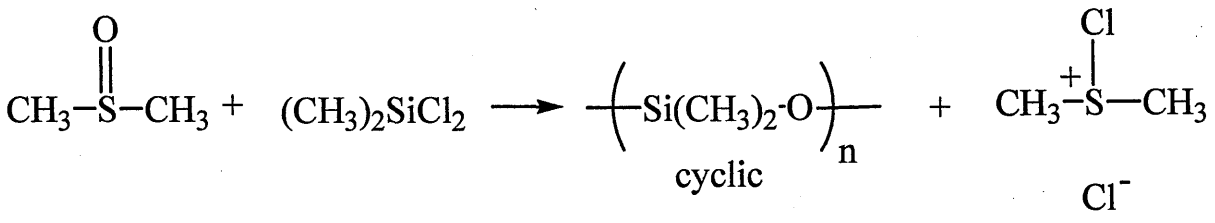


Scheme 3.5 – Unno's route to cage formation.

We thus looked for an alternative method of constructing the T_6 cage that was easy to carry out, used readily available starting materials and was applicable to a wide range of substituents on silicon.

3.6 – "Non-aqueous" hydrolysis of trichlorosilanes: synthesis of T_6 cages.

As described in Chapter 2, the "non-aqueous" hydrolysis of dichlorodimethylsilane using dimethylsulfoxide was first reported in 1965[184] and has subsequently been revisited by Voronkov[187], Weber[188] and Brook[189]. In a recent study, Brook has shown that early in the reaction between $RSiCl_3$ and DMSO, a six membered cyclotrisiloxane, D_3, is formed in good yields.



2.12

Scheme 3.6 - A general scheme of the formation of cyclic siloxane; D_3 if n=3, D_4 if n=4, etc.

Based on the idea that six membered rings are preferred in the "non aqueous" hydrolysis of dichlorosilanes, if trichlorosilanes were employed this should favour T_6 formation, through the ring acting as a template or through the coupling of two such rings, as will be explained later in this thesis.

As reported in Chapter 2, we used a wide range of oxygen donor compounds to condense dichlorosilanes. Thus we decided to react the different oxygen donors with a trichlorosilane. The trichlorosilane chosen was octyltrichlorosilane and it was reacted with DMSO, iodosobenzene, pyridine N-oxide, triphenylphosphine oxide and the trioxysulfur pyridine complex.

When treating dichlorosilanes with oxygen donor compounds we obtained D_3, D_4 and D_5, as discussed in Chapter 2. The ratio of the oxygen donor/ dichlorosilane was 1:1 and therefore it was reasonable to try the same ratio with the trichlorosilanes. Initially we expected to obtain a range of T_6, T_8 and T_{10} silsesquioxane cages in varying amounts. Since DMSO gave the highest ratio of D_3, we expected this reagent to give the highest yield of T_6 cages. ^{29}Si-NMR analysis of the reaction mixtures revealed that the starting material disappeared but no silsesquioxane cages were formed with any the oxygen donor compounds apart from DMSO. This disappearance of the starting material can be explained by the formation of resinous products which leads to a broadened baseline. Such a broadened baseline in the ^{29}Si-

NMR is the result of the formation of a wide range of compounds with numerous silicon environments. The only oxygen donor compound which gave a single peak was DMSO and thus this reagent was used in all further reactions.

A wide range of trichlorosilanes are commercially available for such a synthesis of T_6 cages and Table 3.1 lists the tricholorosilanes we employed. We used trichlorosilanes carrying a wide range of functionalities attached to the silicon atom, such as primary, secondary and tertiary carbon atoms, linear chain and aromatic groups. Some of the trichlorosilanes that were chosen carry a different functionality that does not interfere with the reaction but which could be used for further elaboration. The majority of these trichlorosilanes were commercially available but some were synthesised by hydrosilylation. For example, methyl 3,3-dimethyl-5-trichlorosilylpentanoate was prepared using this methodology.

The "non-aqueous" hydrolysis of trichlorosilanes with DMSO was carried out in choloroform and, initially, a trichlorosilane/DMSO ratio of 1:1 was used, as in the reaction with dichlorosilanes. This ratio gave a very low yield of T_6 and/or other cages, as monitored by ^{29}Si-NMR. Carrying out the reaction using different trichlorosilane/DMSO ratios suggested that a ratio of 1:2 equivalents seemed to be the ideal ratio, giving reasonable yields of T_6.

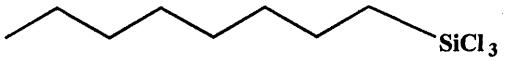
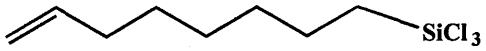
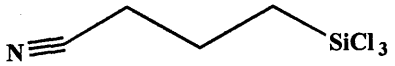
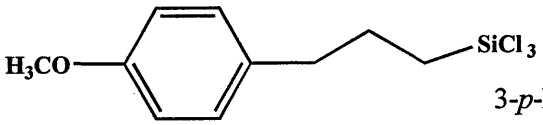
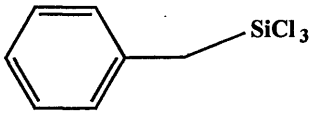
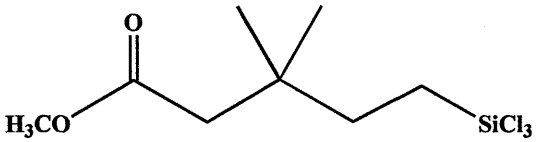
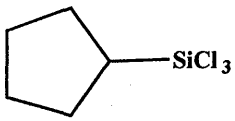
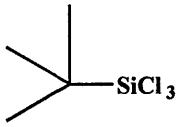
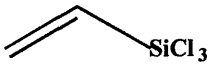
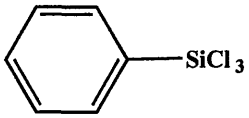
1	$HSiCl_3$	Trichlorosilane
2		Octyltrichlorosilane
3		7-octenyltrichlorosilane
4		Cyanopropyltrichlorosilane
5		3-*p*-Methoxyphenylpropyltrichlorosilane
6		Benzyltrichlorosilane
7		Methyl 3,3-dimethyl-5-trichlorosilylpentanoate
8		Cyclopentyltrichlorosilane
9		Cyclohexyltrichlorosilane
10		*tert*-Butyltrichlorosilane
11	CH_3SiCl_3	Methyltrichlorosilane
12		Vinyltrichlorosilane
13		Phenyltrichlorosilane

Table 3.1- Selection of trichlorosilanes used as starting materials.

The ^{29}Si-NMR of the reaction mixture, after 24 h, exhibited, for the majority of the trichlorosilanes, a characteristic peak in the region –55 ppm to –57 ppm as expected.

This is in agreement with the chemical shifts of previously prepared T_6 cages.[182,186] The corresponding range for T_8 cages is -65 ppm to -67 ppm. The difference in geometry between the four membered ring and the three membered ring leads to a high field shift as observed with D_4 and D_3 rings. The exception to this is phenyl hexasilsesquioxane which has a ^{29}Si chemical shift of -66.89 ppm; this up field shift is typical of a phenyl substituent, again, as observed in the D ring series, due to the sp^2 hybridization of the carbon next to the silicon.

Table 3.2 on page 105 gives the results of our study. We found that the trichlorosilanes (1 equivalent) could be reacted with dimethylsulfoxide (2 equivalents) in chloroform at room temperature (although, an increase in the temperature of up to 45 °C was observed during the addition of every trichlorosilane in the reaction mixture) to give T_6 cages which could be clearly identified by ^{29}Si-NMR.

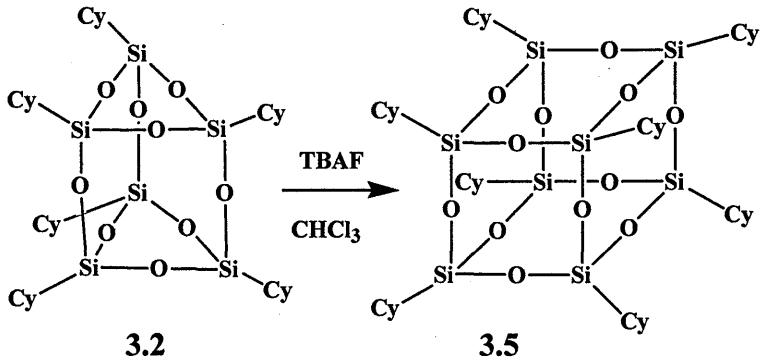
These reactions produce a certain amount of resin along with the product and therefore the T_6 product needed further purification. Several methods have been tried to purify the various T_6 cages from the reaction mixture, including crystallisation. Crystallisation was unsuccessful for the T_6 cages carrying a long carbon chain on the silicon due to the high mobility of the chains which cause them to be reluctant to crystallise in an ordered structure. Any attempt to crystallise such molecules, in particular for the octyl-T_6, gave a wax like solid. Previous studies with T_8 cages has shown it is very difficult to crystallise cages in the presence of resin, because the resin seems to prevent the precipitation of the cage. Successful recrystallisation is only usually achieved after purification using column chromatography.

The purification that appeared to be the most successful was column chromatography. However, when the column was packed with ordinary silica gel and

hexane was used as the eluent, we only obtained the resin, suggesting the cage was destroyed on the column. Despite using a range of polar solvents we were never able to retrieve the T_6 cage from the column. As explained in Chapter 2, D_3 rings are the only molecules of the D series to have a ring strain energy and therefore they are generally unstable and the silicon atom is much more susceptible to nucleophilic attack compared to other D rings. This means that D_3 rings readily rearrange themselves into larger (and more stable) rings in the presence of nucleophilic reagents. We have subsequently used this enhanced reactivity of T_6 cages to insert T silicon atoms with a different functionality to make mixed T_8 cages and T_6D_2 cages[195,205]. Silica gel consists of silicon oxide and a consequence of its structure is that it has nucleophilic oxygens (O^-) on the surface. These oxygens act as nucleophiles reacting with the silicon on the T_6 cage and thus destroying it. Previous work has shown that other cages such as T_8, T_{10} and T_{12} can be readily separated by column chromatography using silica gel, however, they are not so prone to nucleophilic attack.

A great deal of time was spent discovering the best procedure for the purification of T_6 cages. The first attempts at purification of the T_6 cages were carried out using the stationary phases readily available in the laboratory: neutral silica gel, acid washed and base washed silica gel as well as alumina. Only acid washed silica gel seemed to give any sign of the T_6 cage.

T_6 cages have proved to be very delicate and it is clear that isolation and purification requires careful and controlled handling. In fact T_6 cages can be readily rearranged to T_8 cages. Yang[195] has shown that once a T_6 (**3.2**) cage is synthesised with DMSO, it can be easily converted into the T_8 (**3.5**) cage simply by treating the cage with TBAF, as shown in Scheme 3.7, confirming that these are indeed delicate structures.



3.2 3.5

Scheme 3.7 – Rearrangement of T_6 into T_8 cage.

In order to deactivate the oxygens on the surface of the silica gel, the solid silica was treated with chlorotrimethylsilane to cap any reactive centres. However, we had to determine the optimum percentage that would create the right balance between the need for the cage to pass through without being converted into resin and the need for the cage to adhere to the surface and thus achieve a good separation.

A process of trial and error to obtain the ideal amount of TMS-Cl so that the right number of oxygens on the surface of the silica are deactivated, suggested a TMS percentage in the range between 2.5% and 10%.

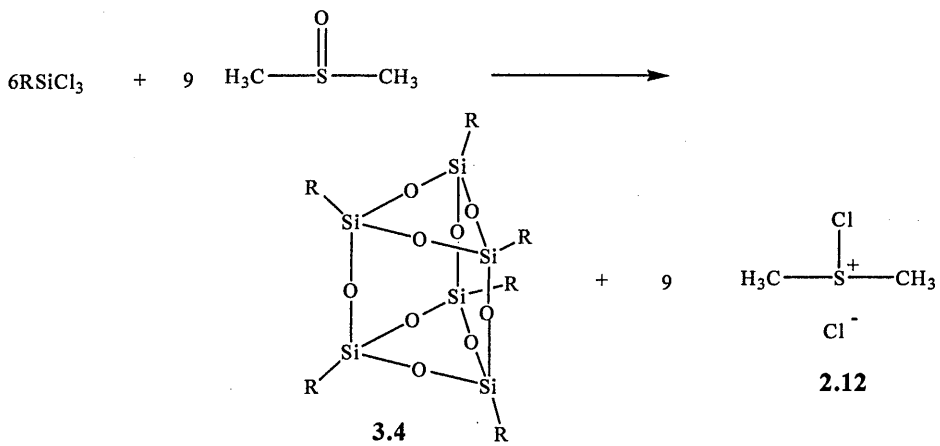
For example, a mixture prepared using 50 g of silica gel suspended in 100 ml of chloroform and containing 10% (by weight) of TMS-Cl, was used to pack a chromatography column and used to elute the reaction mixture using $CHCl_3$ as eluent (after washing out any unreacted TMS-Cl). A ^{29}Si-NMR of the fractions containing the product, suggested that no separation had occurred. On the other hand when we repeated the same procedure using 2.5% or 3% TMS-Cl (by weight) to treat the silica gel followed by elution with hexane, the ^{29}Si-NMR of the product fractions, exhibited the characteristic pattern of a resin and no peak was observed in the T_6 region.

We found that the optimum percentage was 5% (by weight). Such a percentage ensures that the correct number of active oxygen species are free to guarantee the

separation of the cage from the resin but that the more nucleophilic oxygens are capped to preserve the cage from breaking. However, some cages (especially those with linear alkyl chains) had to be purified using alumina.

All yields quoted in Table 3.2 are isolated yields after purification using an alumina column or a silica gel column treated with chlorotrimethylsilane. In all cases the trichlorosilane/oxygen donor ratio used was 1:2 and, as for the dichlorosilanes, the reactions were performed in chloroform. To understand the process by which the T_6 cages are built up, the reaction mixture was analysed using ^{29}Si-NMR spectroscopy at different times. The initial spectra, recorded after a few hours of reaction, showed that the starting material was no longer present in the reaction mixture, but in these early stages, no T_6 or other compounds were detected in its place.

As discussed earlier, the use of oxygen donor compounds other than DMSO, led to poor yields of D_3. We suggest that a D_3 ring is probably the intermediate product in the T_6 formation. If the D_3 ring is produced in low yield, the yield of the T_6 cage will also be affected. In all cases, where alternative oxygen donors were used, the yield of T_6 is probably too low to be detected by ^{29}Si-NMR. In fact, DMSO was the only reagent that gave isolable quantities of cage compounds with trichlorosilanes.



Scheme 3.8 – A general reaction of the "non-Aqueous" hydrolysis of trichlorosilanes.

Table 3.2 shows that, as expected, compact substituents such as phenyl, cyclopentyl and cyclohexyl give solid T_6 cages in good yields whereas small substituents gave mainly resins.

Starting Trichlorosilane	**^{29}Si-NMR /ppm**	**Physical State of T_6 product**	**Yield /%**
Octyltrichlorosilane	-54.18	Gel	24.45
tert-Butyltrichlorosilane	-56.78	Resin	---
Vinyltrichlorosilane		Resin	---
3-Cyanopropyltrichlorosilane	-55.46	Oil	
Phenyltrichlorosilane	-66.89	Solid	
Benzyltrichlorosilane	-59.02	Oil	
Cyclohexyltrichlorosilane	-56.60	Solid	10.41
Cyclopentyltrichlorosilane	-54.37	Solid	9.36
iso-Butyltrichlorosilane	-55.42	Solid	11.00
7-Octenyltrichlorosilane	-54.25		
Methyl 3,3-dimethyl-5-trichlorosilylpentanoate	-56.62	Oil	6.3
3-(*4*-Methoxyphenyl) propyltrichlorosilane	-54.42	Solid	6.4
5-(Bicycloheptenyl)trichlorosilane		Resin	---
Trichlorosilane		Resin	---
Methyltrichlorosilane		Resin	---

Table 3.2 - Yields and properties of T_6 cages prepared by the "non aqueous" hydrolysis of trichlorosilanes using DMSO.

Surprisingly primary alkyltrichlorosilanes such as propyl, octyl and methyl 3,3-dimethyl-5-trichlorosilylpentanoate still gave T_6 cages in reasonable yields and this represents the first synthesis of this important class of compound.

Octyl-T_6 (3.6). Octyl trichlorosilane was the first starting material used to perform the "non-aqueous" hydrolysis using DMSO as the source of oxygen. The results of this reaction were very encouraging. The ^{29}Si-NMR of the reaction mixture, recorded after 24 h of reaction, displayed a sharp single resonance with a chemical shift of –54.18 ppm. Further purification using a chromatography column packed with alumina, gave a gel like product.

Despite numerous attempts to crystallise the octyl-T_6 using pure hexane and a mixture of chloroform and hexane, we were unable to obtain a good crystal of the T_6 cage. The reason for this was believed to be because free rotation of the linear hydrocarbon chain does not allow the molecule to pack in an ordered structure. ^{1}H-NMR and ^{13}C-NMR, however, confirmed the purity of the product. The proton NMR displayed three major resonances with chemical shifts of 0.10 ppm, 0.36 ppm and 0.74ppm; the carbon NMR shows eight resonances corresponding to the carbons in the octyl chain with chemical shifts of: 11.36 ppm, 14.07 ppm, 22.28 ppm, 22.65 ppm, 29.23 ppm, 30.85 ppm, 31.91 ppm and 32,54 ppm. Both proton and carbon NMR spectra were recorded in $CDCl_3$.

7-Octenyl-T_6 (3.7) and **Cyanopropyl-T_6 (3.8).** As mentioned earlier, the aim of using trichlorosilanes with different functionalities was to use them to perform other reactions such as the condensation of cages to give polymer like structures and/or to form dendrimers via hydrosilylation. The 7-octenyltrichlorosilane and the cyanopropyltrichlorosilane were chosen because, as well as containing a linear chain of hydrocarbons they also contain unsaturated carbon atoms.

The reaction with 7-octenyltrichlorosilane and cyanopropyltrichlorosilane was performed using the same procedure as for the other trichlorosilanes. After 24 hours of reaction the ^{29}Si-NMR displayed a peak with a chemical shift of –54.25 ppm for the 7-octenyl-T_6 and –55.46 ppm for the cyanopropyl-T_6. In both cases the NMR was very clean suggesting little further purification was needed. We nevertheless tried to purify them using a chromatography column packed with alumina, which previous studies had suggested was the best support. However, analysis of the fractions from the column suggested that the cages had been converted to resin.

3-(4-Methoxyphenyl)propyl-T_6 (3.9). We obtained one of our most significant results using 3-(4-methoxyphenyl)propyltrichlorosilane. The "non aqueous" hydrolysis of this linear trichlorosilane gave the corresponding T_6 as shown in Table 3.2. The table also reports the physical state of all the T_6 cages obtained and, unlike the majority of T_6 cages having a linear chain attached to the silicon atom, the 3-(4-methoxyphenyl)propyl-T_6 is a solid. We were subsequently able to recrystallise the solid and analyse it by X-ray diffraction.

Normally, when a linear chain is attached to the silicon atom in a T_6 or a T_8 cage, one would expect that the chains form an "octopus" like molecule where the cage represents the core and the arms radiate from it in all directions and are free to move around. The X-ray structure is reported in Figure 3.1. The crystal structure of 3-(4-methoxyphenyl)propyl-T_6 suggests that it is a surprisingly ordered structure where the arms are aligned along the main axis of the cage, rather than equally distant from each other, pointing in all possible directions. Full details of the X-ray crystal structure, as well as other views of the structure, are reported in the appendices.

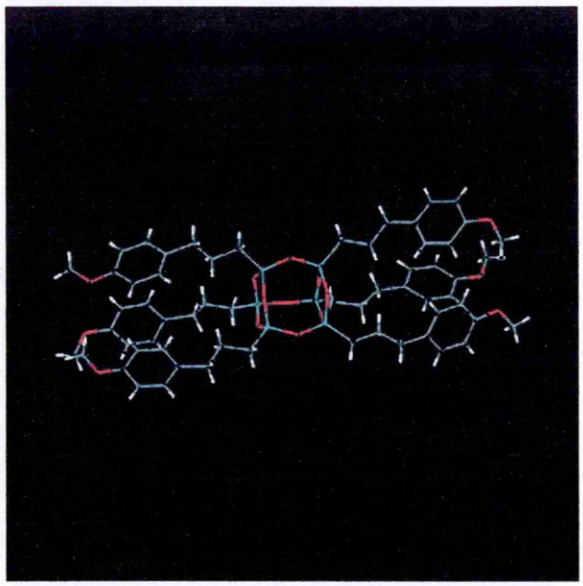


Figure 3.1 – Crystal structure of 3-(4-methoxyphenyl)propyl-T_6 (**3.9**).

So far the only T_6 crystal structures that have been published are cyclohexyl-T_6[196] and cyclopentyl-T_6[195] and *iso*butyl-T_6[181]; a comparison of selected bond lengths and angles is shown in Table 3.3 which highlight the very little differences in the Si—O bonds within the cage and the Si and the substituents.

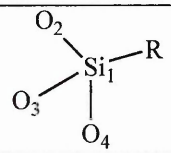
		Cy-T_6 (Molloy)	Isobut-T_6 (Feher)	3-(4-methoxyphenyl)propyl-T_6 (Maesano)
Lengths	Si_1—R	1.837	1.810	1.840
	Si_1—O_3	1.643	1.640	1.636
	Si_1—O_4	1.626	1.628	1.627
	Si_1—O_2	1.634	1.628	1.635
Angles	O_4—Si_1—R	108.3	110.7	108.7
	O_2—Si_1—O_3	106.8	106.3	106.0
	O_3—Si_1—O_4	109.4	108.5	108.3
	O_2—Si_1—O_4	109.2	109.0	108.9

Table 3.3 – Selected bond lengths and angles of T_6 compounds.

The only data concerning T cages containing phenyl groups were reported in 1998 by Feher[181] who published the crystal structure of phenyl-T_8. In this crystal structure

the phenyl groups are orientated as far away as possible from one another as expected. A schematic representation of the orientation of the phenyl groups in this T_8 cage is shown in Figure 3.2, where the square represents a face of the T_8 cage and the lines the profile of the phenyl rings.

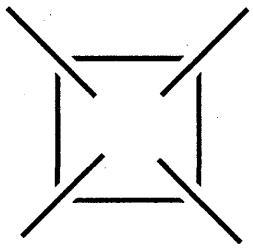


Figure 3.2 – A perpendicular orientation of the phenyl group with respect to the T_8 cage.

The same type of representation can be used in the case of the 3-(-4-methoxyphenyl)propyl-T_6 cages as shown in Figures 3.3 and 3.4:

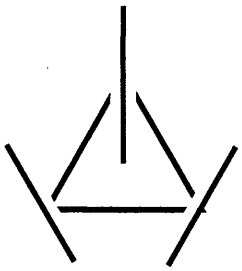


Figure 3.3 – One possible orientation of the phenyl group with respect to the T_6 cage.

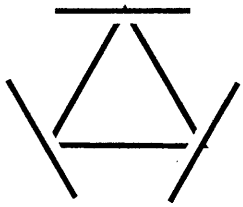


Figure 3.4 – A different orientation of the phenyl group with respect to the T_6 cage.

Again we assume that the triangles represent a section of the T_6 cage and the lines the profile of the phenyl substituents. In this case the cage is observed from the upper face in Figure 3.4 and from the bottom face in Figure 3.3. The first difference between the T_6 and T_8 in the disposition of the phenyl groups is that, in the T_6 cage they are disposed facing each other on one side and parallel with each other on the other side. In the T_8 cage they are all orthogonal. A similar representation to that given for the T_6 can also be used for the T_8 cage. In the T_8 structure the phenyl rings show the same disposition both in the upper layer as well as in the lower layer as shown in Figure 3.4

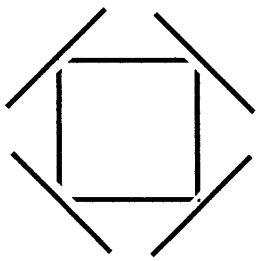


Figure 3.4 – The phenyl groups on a T_8 cage could be orientated facing one another.

This difference in the disposition of the phenyl groups possibly arises from the free rotation within the propyl chain.

In 2001 Yang reported the crystal structure of 3-(4-methoxyphenyl)propyl-T_8 obtained by treatment of the corresponding T_6 with TBAF. It is interesting to compare the two structures. Figures 3.5 and 3.6 show the X-ray crystal structures of 3-(4-methoxyphenyl)propyl-T_6 and 3-(4-methoxyphenyl)propyl-T_8 respectively. Table 3.4 summarises the most significant angles in the T_6 and T_8 cage.

A close analysis of the crystal structure of 3-(4-methoxyphenyl)propyl-T_6, does not highlight many major differences to that of the 3-(4-methoxyphenyl)propyl-T_8, in terms of bond angles in the arms and, more surprisingly, no significant differences are encountered in the bond lengths in the cages.

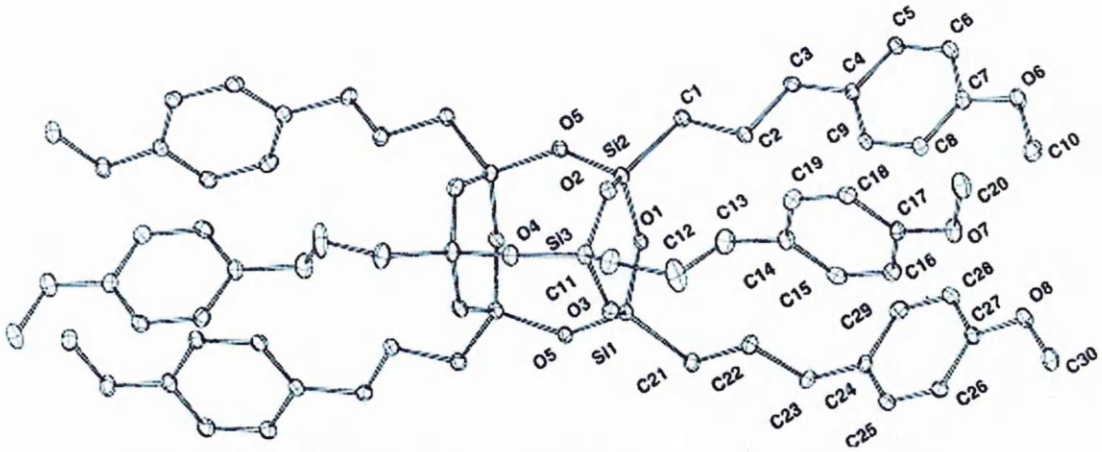


Figure 3.5 – Crystal structure of 3-(4-methoxyphenyl)propyl-T_6

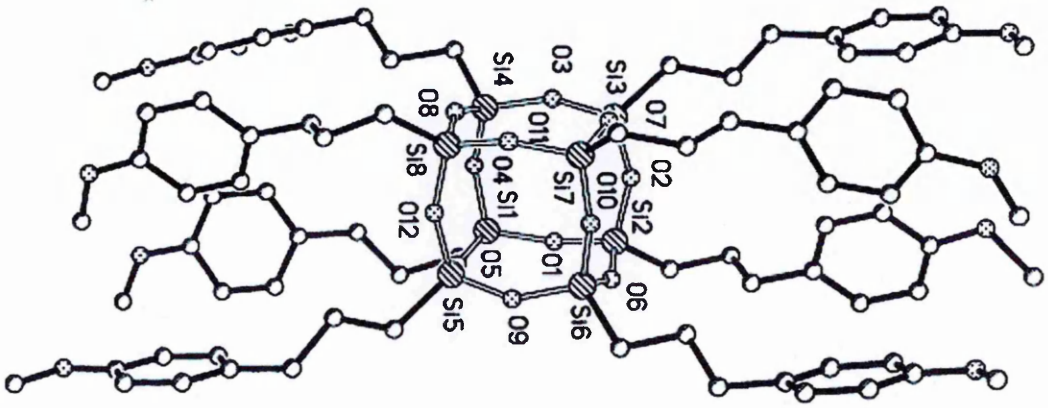


Figure 3.6 - 3-(4-methoxyphenyl)propyl-T_8 reported by Yang[195].

3-(4-methoxyphenyl)propyl-T_6	3-(4-methoxyphenyl)propyl-T_8
O1—Si2—O2 105.37(12)	O6—Si6—O10 108.6(2)
Si2—O4—Si3 132.16(3)	Si3—O2—Si2 150.9(3)
Si3—O4—$Si3^I$ 142.4(2)	Si5—O9—Si6 146.1(3)

Table 3.4 – Significant angles in 3-(4-methoxyphenyl)propyl-T_6 and T_8.

The angle marked in red is the most significant difference between the two cages. As expected, the angle in the "T_3" ring of the T_6 structure is less than in the "T_4" ring of the T_8 cage. A reduction in the Si-O-Si bond angles is necessary to accommodate the

ring size and it is interesting that, again as expected, it is the oxygen that provides the flexibility rather than the bond at silicon.

This particular type of structure is characteristic of cages that act as liquid crystals.

A typical liquid crystalline silsesquioxane has the general structure shown in Figure 3.7;

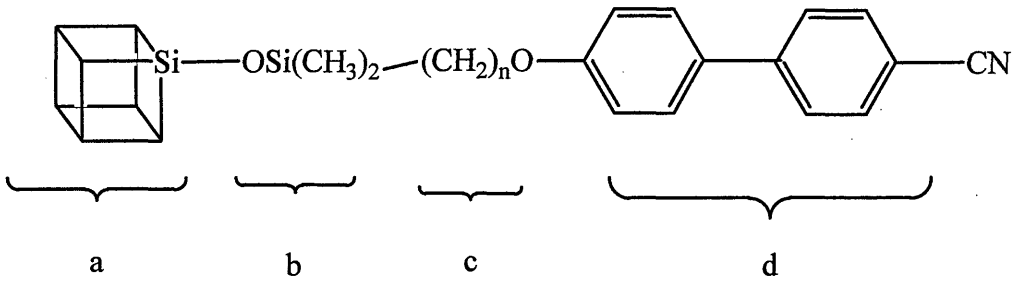


Figure 3.7 - A typical structure of a liquid crystalline silsesquioxane.

It consists of a silsesquioxane cage, the central body of the molecule (a), to which the mesogens are attached at each corner. To act as liquid crystal, the arms in the cage must meet certain requirements: they must contain a hydrocarbon spacer (c) linking the mesogen (d) to the silicon cage; such a linkage can also contain an organosilicon spacer unit (b).

These types of liquid crystals are normally prepared in two steps: the first step involves the synthesis of the cage. The arm, which is synthesised separately, is then attached in a subsequent reaction, usually through hydrosilylation.

The propyl chain of the 3-(4-methoxyphenyl)propyl arm acts as spacer placing the phenyl groups far enough from the cage for them to reach an arrangement where the arms are aligned. The driving force for this is the Van der Waals interactions between the three arms in the T_6 cage or the four arms in a T_8 cage, together with specific interactions between the aromatic groups.

The analysis of the liquid crystalline properties of such cages was not part of this project, but it would be interesting, as further work, to verify if such molecules display liquid crystalline behaviour.

The particular structure exhibited by the 3-(4-methoxyphenyl)propyl-T_6 cage could not be observed with any of the other T_6s which had linear chains as the arm. Perhaps, in other cases the arms spread out radially from the core, suggesting the phenyl interactions may have been important in keeping the chains together. The extreme mobility of the arms around the cage probably lead to the huge difficulties encountered in separating these T_6 cages as crystalline materials. Apart from the octyl-T_6, which gave an oil like pure product, it was not possible to isolate pure samples of any other cages carrying a linear alkyl chain.

Benzyl-T_6 (3.10). As shown in Table 3.2 Benzyl-T_6 was not obtained as a pure compound and therefore the yield could not be calculated. An oil like product was obtained by column chromatography using silica gel treated with 5% TMS-Cl. The ^{29}Si-NMR of the oil showed a little resin.

Despite the presence of only a phenyl group, the behaviour described for the 3-(4-methoxyphenyl)propyl-T_6 was not observed with the benzyl-T_6, probably because the single $-CH_2-$ group is not a sufficiently large spacer to provide flexibility. Benzyl-T_6 thus did not give a crystalline compound.

***t*-Butyl-T_6 (3.11)**. In contrast to the Matsumoto route, we were unable to isolate T_6 cages via DMSO "hydrolysis" when bulky substituents such as *tert*-butyl were employed. In this case a range of products were observed which were probably D polyol rings.

According to the Matsumoto[186] paper, the ^{29}Si chemical shift of *tert*-butyl-T_6, recorded in benzene, is –54.3 ppm. Using the DMSO methodology we observed

several resonances, including a peak in the T_6 region (chemical shift of –56.78.ppm in $CDCl_3$) which probably corresponds to the *t*-butyl-T_6. A series of other resonances was observed; one had a chemical shift of –8.7 ppm, and a small series of resonances was seen in the range –29.6 ppm to –31.6 ppm and a second series of peaks was observed in the range –46.6 ppm to –48.2 ppm, with a major resonance with a chemical shift of –48.0 ppm.

As mentioned in Chapter 2 the mechanism proposed for this type of hydrolysis involves the formation of linear and cyclic intermediates; of course, several isomers of each intermediate (linear and cyclic triol) may be formed. The resonance in the region of –29.6 ppm to –31.6 ppm may well arise from the different isomers of the linear triols. Similarly the resonances in the region between –46.6 ppm to –48.2 ppm could also be attributed to the isomers of the linear triols or tetrol polysiloxane. The presence of a predominant resonance suggests that one isomer is preferred in comparison to the others. The fact that the *tert*-butyl-T_6 is formed in such small amounts suggests that the preferred isomer of the "T_3" and "T_4" rings is the *trans* form due to the presence of the bulky substituents. Finally, the fact that the chemical shift of *tert*-butyl-T_6 isolated in this method differs from that published by Matsumoto by about 2 ppm is not surprising considering the possible interactions with the numerous compounds present in the mixture as well as the different solvent used to obtain the spectra: benzene in the work of Matsumoto and chloroform in our work.

Hydrogen-T_6 (3.12), methyl-T_6 (3.13) and vinyl-T_6 (3.14). Cage structures were not produced with small substituents. For example, vinyltrichlorosilane gave no identifiable products. Chan has shown that $HSiCl_3$ reduces DMSO to dimethylsulfide and thus, it was not surprising that we obtained no cages in this instance[190]. Perhaps

surprisingly, whilst we have been able to form D_3 and D_4 rings from CH_3SiHCl_2 using DMSO, use of this reagent with trichlorosilane led to a complex mixture of products. NMR analysis of the reaction mixtures when methyl or vinyl trichlorosilanes are used gave a broad peak in the ^{29}Si-NMR in the T_6 region rather than in the T_8 region. This confirms that D_3 rings are preferentially formed, but further condensation leads to resin rather than ordered cages.

Phenyl-T_6 (3.15). The phenyl-T_8 cage can be readily synthesised by the conventional hydrolysis method. Of all the T_8 cages we have prepared, this is the only one that exhibits a very low solubility in chloroform and is completely insoluble in all other solvents and thus it is difficult to record its ^{29}Si-NMR. A search of the literature suggests that phenyl-T_6 has never been synthesised previously. As shown in Table 3.2, the "non-aqueous" hydrolysis of phenyltrichlorosilane gives a resonance in the ^{29}Si-NMR spectrum with a chemical shift of –66.8 ppm. Most of the trichlorosilanes employed carry an sp^3 carbon next to the silicon; in the case of phenyltrichlorosilane, the carbon next to the silicon was sp^2 hybridised. This moves the chemical shift by about 10 ppm towards higher field (and therefore lower chemical shift), and thus a value of –66.7 ppm for Ph-T_6 is to be expected if the corresponding R_6T_6, with alkyl sp^3 carbon, occur at –56 ppm.

Phenyl-T_8 could be easily separated from the other reaction products because of its low solubility. However phenyl-T_6 is more soluble in most solvents. Furthermore, mixing of the desired product with resin makes the isolation even more complicated, because, as with other T_6 or T_8 cages, the resin acts as good solvent for the cages themselves preventing crystallisation.

Despite the NMR spectrum displaying a sharp single peak indicating the presence of a single product in "high" yield, all of the many attempts to isolate the phenyl-T_6

cage as a pure product failed. Considering the very low solubility of phenyl-T_8 in most organic solvents, we had assumed that phenyl-T_6 would exhibit the same type of behaviour. However, we found that phenyl-T_6 is very soluble in chloroform (the reaction was performed in chloroform and this was used to record the ^{29}Si-NMR) and no precipitate was observed. This suggests that the geometry/dimensions of the cage play an important role in its solubility.

Phenyl-T_8 was found to have a highly ordered structure, therefore the same type of structure was expected for the corresponding T_6. We thus tried to isolate the phenyl-T_6 by recrystallisation. All solvents and combination of solvents available in the laboratory were used to recrystallise the cage but no crystals were ever observed. For example a solution of the reaction mixture obtained after washing with water, in order to remove the HCl formed and the by-products formed from DMSO, was dissolved in hexane (where phenyl-T_8 is completely insoluble) but after several weeks (some solutions were left for months) of slow evaporation of the solvent no crystal formation was observed. We also tried to dissolve the cage in the minimum of hot solvent but this led to the breaking of the cage (confirmed by a classic broad peak in the ^{29}Si-NMR).

Phenyl-T_6 could not be isolated by chromatography using columns packed with ordinary silica gel as well as using silica gel treated with trimethylchlorosilane. Alumina was also used as the column packing but this was still unsuccessful. Table 3.5 shows a list of the solvents and mixture of solvents used for the purification of phenyl T_6 used for recrystallisation and as chromatography eluent:

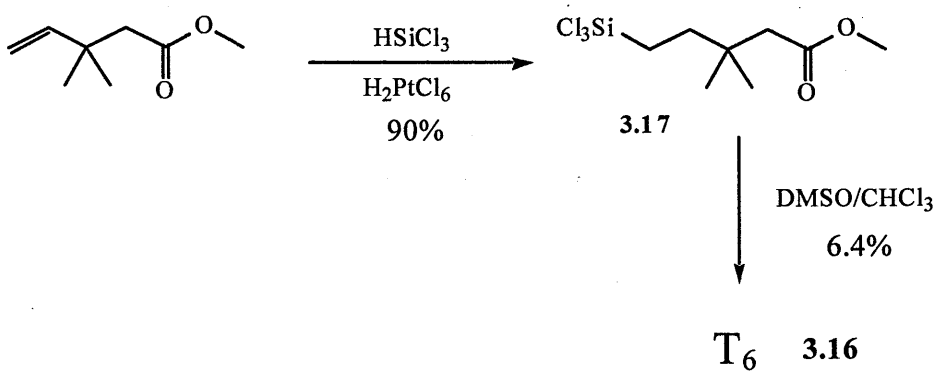
Solvent	Mixed Solvents
Hexane	Hexane/CH_3OH
CH_3OH	
CH_3Cl	

Table 3.5 – Solvents used for purification of Phenyl-T_6.

The ring strain energy may explain why, with the possible exception of cages carrying a linear chain as the arm, the majority of the T_6 cages could not be isolated using column chromatography, since they decomposed so readily.

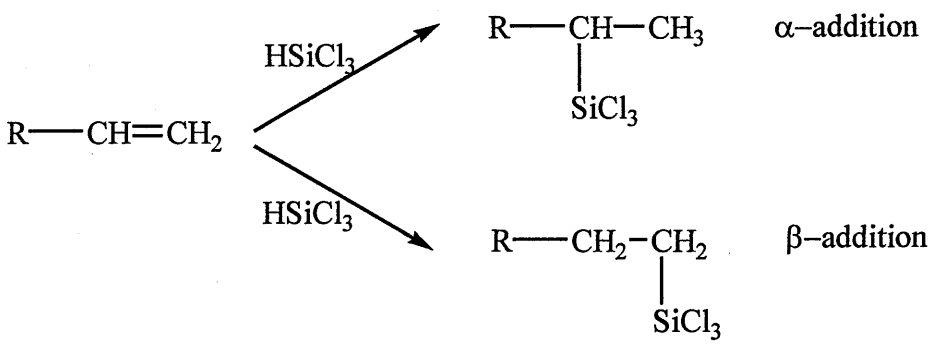
Pourny has recently carried out thermogravimetric analysis (TGA) on a range of silsesquioxane cages[209]. He found that a sample of T_6 cage prepared in this work underwent sublimation at about 300°C. This surprising result suggests that in the absence of nucleophiles and in the presence of an inert atmosphere, T_6 compounds are quite stable, even at high temperatures. Thus, we now believe that we can improve upon the yields given in Table 3.2 by subliming the T_6 products from the reaction mixture. This will not only provide a route to purer products but may also lead to crystals to enable us to carry out single crystal X-ray analysis.

3,3-dimethyl-4-methoxycarbonyl(butyl)-T_6 (3.16). Our previous strategy for preparing organooctasilsesquioxanes relied on the synthesis of the alkene arm followed by attachment to octahydrosilsesquioxane by hydrosilylation.[180] While we could not use this approach for T_6 because H_6T_6 could not be isolated, we have been able to transfer this methodology to T_6 synthesis through initial hydrosilylation of the alkene with trichlorosilane followed by reaction with DMSO. For example, as shown in Scheme 3.9, hydrosilylation of methyl-3,3-dimethylpent-4-enoate using chloroplatinic acid gives the corresponding trichlorosilane derivative, **(3.17)**, in about 90% yield and thence the T_6 derivative in 6.4 % yield.



Scheme 3.9 – The two-step route of the formation of 3,3-dimethyl-4-methoxycarbonyl(butyl)-T_6.

The hydrosilylation is normally carried out in the absence of solvent. The trichlorosilane is added to the methyl-3,3-dimethylpent-4-enoate in the presence of a 0.02 M solution of hexachloroplatinic acid in isopropanol and the solution is stirred under nitrogen to prevent the hydrolysis of the trichlorosilane by water in the atmosphere. The reaction was followed by infrared spectroscopy, monitoring the disappearance of the peak at 2250 cm^{-1} corresponding to the stretching of the Si-H bond. This took about four hours. The ^{29}Si-NMR chemical shift of the methyl 5-tricholorosilyl-3,3-dimethylpentanoate was –13.8 ppm. As with other linear terminal alkenes only β-addition is observed as displayed in Scheme 3.10:



Scheme 3.10 α- or β-addition of the $SiCl_3$ group in hydrosilylation.

Because the methyl 5-tricholorosilyl-3,3-dimethylpent-4-enoate cannot be stored for a long time, since, like other trichlorosilanes, it is susceptible to hydrolysis, it was

used straight after its synthesis without further purification. The presence of other by-products and the catalyst do not interfere with the reaction with DMSO; especially since the amount of the catalyst, compared to the amount of the reagents, is very small.

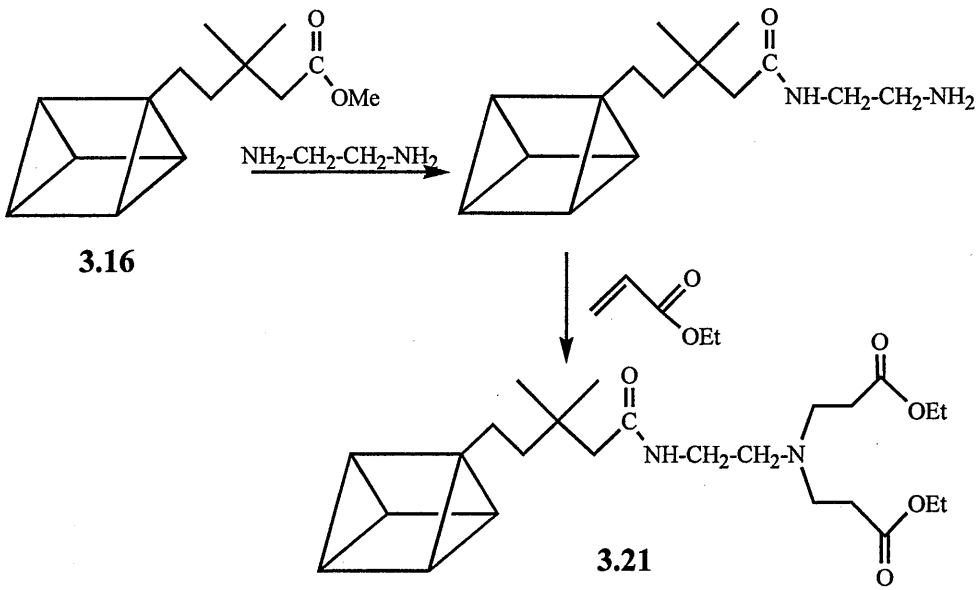
Cyclopentyl-T_6 (3.18) and cyclohexyl-T_6 (3.19). When cyclohexyltrichlorosilane or cyclopentyltrichlorosilane were reacted with DMSO, the ^{29}Si-NMR analysis gave, in both cases, a single sharp resonance, the chemical shifts of which were of –56.60 and –54.37, respectively. Cyclohexyl and cyclopentyl-T_6 and cyclohexyl and cyclopentyl-T_8 have already been synthesised and characterised by Feher and co-workers[182] although they synthesised these compounds using different methods. It was thus easy to characterise these T_6 compounds formed by our route. The reactions were performed, as for the others, using a ratio trichlorosilane/DMSO of 1:2 and the crude mixture was eluted through a chromatography column packed with neutral alumina and using chloroform as eluent. After crystallisation of the eluted product in hexane, crystals were obtained with a melting point of 264°C for the cyclohexyl-T_6 and 153°C for the cyclopentyl-T_6; the sharp melting points were indicative of the purity of these compounds.

***iso*-Butyl-T_6 (3.20).** *iso*-Butyltrichlorosilane contains a primary carbon attached to the silicon atom and it represents the smallest chain to give a T_6 compound; midway between the methyl group, which did not give any isolable T_6, and the octyl group which gave isolable products in good yield, but in a form of a gel. *iso*-Butyltrichlorosilane was treated with DMSO and the ^{29}Si-NMR recorded after 24 h, which displayed a sharp resonance at –52.42 ppm. The pure product was isolated in 11% yield by eluting the crude mixture through a column packed with silica gel treated with TMS-Cl. As with the octyl-T_6, the *iso*-butyl-T_6 did not form a crystalline

solid and therefore it was not possible to obtain on X-ray structure. Nevertheless, the ^{29}Si, ^{1}H and ^{13}C NMR analysis confirmed the presence of a single product. The ^{1}H-NMR showed resonances at δ_H 0.63 ppm, 0.96 ppm and 1.78 ppm and the ^{13}C-NMR showed resonances at δ_C 22 ppm, 23.8 ppm and 25.6 ppm all characteristic of an *iso*-butyl group.

3.7 – Routes to functionalised T_6 cages.

As with the T_8 cages, we are interested in preparing polyfunctional cages and dendrimers. This requires the synthesis of a cage with a functionality on the arm. Table 3.2 shows that we have been able to produce T_6 cages with pendant alkene, cyano and ester groups which are available for further reactions. For example, the methyl dimethylpentanoate derivative **3.16** could be reacted with ethane1,2-diamine followed by methyl acrylate, as shown in Scheme 3.9, to give the dendrimer with twelve ester groups, as has been carried out with the corresponding T_8 cage.



Scheme 3.9

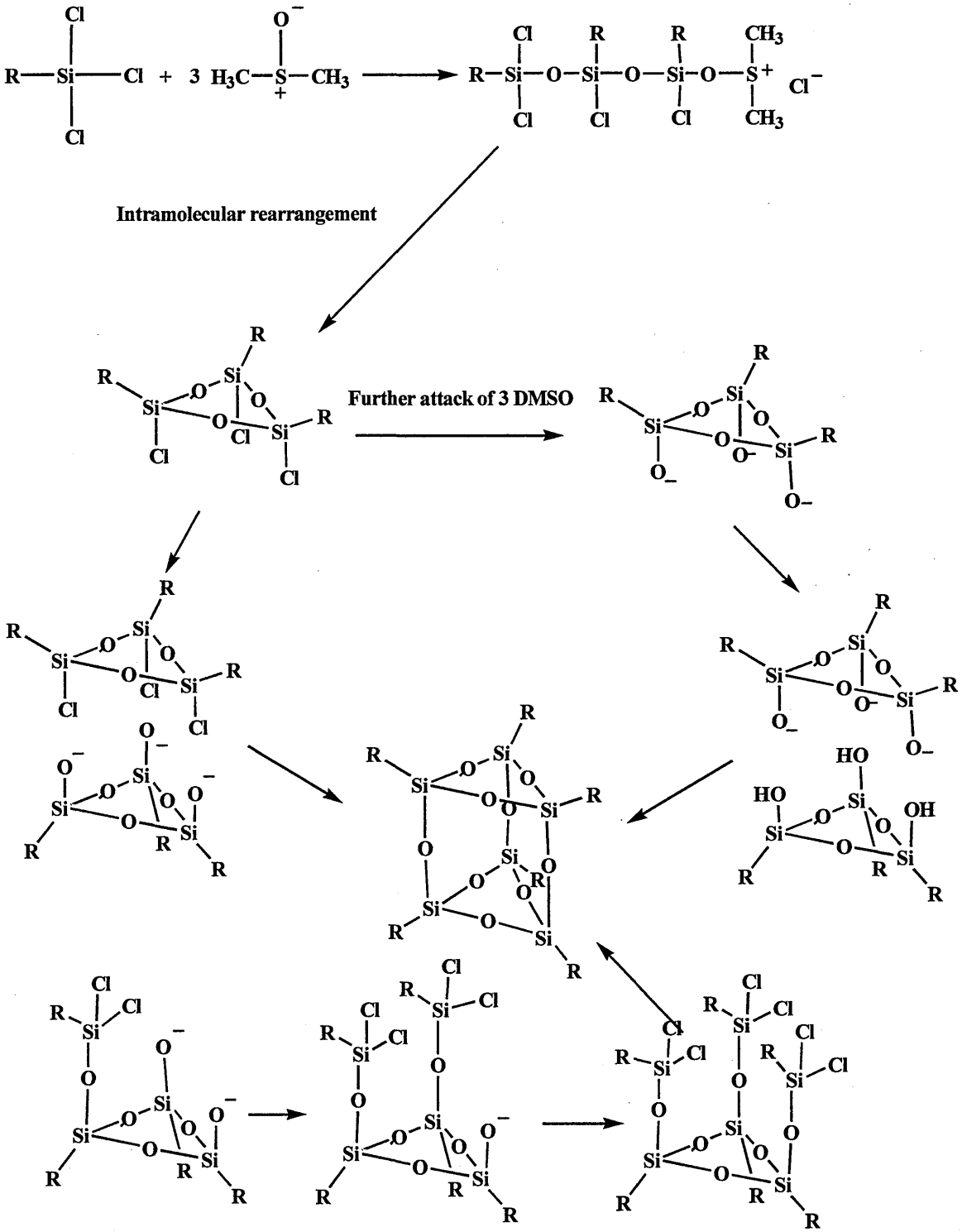
In conclusion we have developed a robust method for the synthesis of T_6 cages in reasonable yield with a wide range of substituents. This should lead to the increased availability of T_6 structures that can be used in exactly the same way that T_8 cages are deployed for building octopus molecules and dendrimers.

3.8 - Formation of R-T_6: the proposed mechanism.

As discussed in Chapter 2, the most likely mechanism of "non-aqueous" D_3 ring formation is the one proposed by Brook. In this mechanism, formation of D rings occurs via linear α,ω–chlorosiloxanes which subsequently undergo intermolecular and/or intramolecular reactions. Intermolecular reaction leads to a linear oligomer which can form longer polymers if the oligomers react together. Alternatively formation of D_n rings (where n = 3-6) occurs via intramolecular reaction of the oligomers and D_3 is the kinetic product of such a reaction.

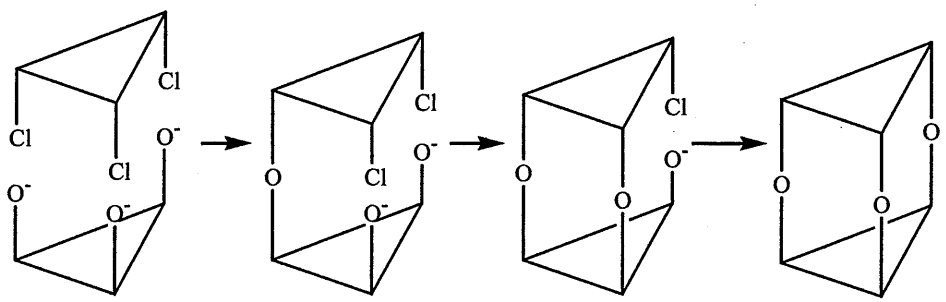
A similar mechanism can be proposed for the formation of T_6. Scheme 3.10 shows the formation of linear oligomers by condensation of more than one chlorosilane with DMSO. The intermediacy of the linear/cyclic chlorosiloxane was confirmed by the ^{29}Si resonance around –29 ppm obtained during reaction of *tert*-butyltrichlorosilane and the intermediacy of the linear and cyclic triols was confirmed by the resonance at around δ_{Si} –48 ppm. Presumably these resonances are only seen when the *tert*-butyl group was the substituent because its bulky group slows down the reaction. Again, DMSO drives the reaction towards the formation of the kinetic product, the D_3 ring. The experiments described in Chapter 2 demonstrated that, using a dichlorosilane with two different substituents on the silicon atom showed no preference towards one isomer compared to the others.

Thus whilst the all *cis* form is drawn in Scheme 3.10 the *trans* isomer is also likely to be formed, but may not lead to T_6 formation.



Scheme 3.10

The *cis*-polychlorotrisiloxane can undergo further reaction with the DMSO to form the *cis*-trisiloxanesilanolate. This can then react quickly with a molecule of the *cis*-polychlorotrisiloxane (or the corresponding triol) via a nucleophilic attack forming the T_6 cage. Of course this will probably happen in a stepwise fashion, forming the monosiloxane followed by reaction to form the other two linkages, according to Scheme 3.11.



Scheme 3.11

Alternatively the T_3 ring can act as a template, first forming the monochlorosilanolate, then the dichlorosilanolate and then the trichlorosilanolate. Subsequent reaction with DMSO would then lead to cyclization to form the cage. Such a stepwise route may not have such strict stereochemical requirements providing inversion at one of the silicon atoms can occur readily.

Since the formation of the trichlorosiloxane and the trisilanolate will have no preference for the all *cis* isomers, and there is the competing possibility of forming linear and/or a cross linked polymers, the yield of T_6 will be very low, as observed.

3.9 - Estimation of T_6 chemical shift. Marsmann's equation.

Since few T_6s are known, there are little ^{29}Si-NMR data reported in the literature and thus it is often difficult to assign the chemical shifts of such compounds. The ^{29}Si-

NMR chemical shift of a T_x cage depends upon several factors such as the substituents on the silicon atom as well as the dimensions of the cage itself. Marsmann and co-workers developed a method to estimate the chemical shift of an unknown T_x cage from the chemical shift of the corresponding T_8 cage. According to Marsmann's paper, published in 1997, the chemical shift of a T_{10} and a T_{12} cage can be calculated from the chemical shift of the T_8 cage by the following equations[210]:

1) $\delta_{T10} = 1.28\ \delta_{T8}$

2) $\delta_{T12A} = 1.25\ \delta_{T8}$ $\qquad$ $\delta_{T12B} = 1.064\ \delta_{T8}$

For the T_{12} cage two equations are necessary because of the two different silicon environments in T_{12}.

In this work we have prepared a range of T_6 cages and measured their ^{29}Si-NMR chemical shifts. Thus, for the first time we are able to correlate the chemical shifts of the T_6 cages, synthesised in our laboratory and the corresponding T_8 cages carrying the same substituent on the silicon atom. It is possible to write an equation, similar to that found by Marsmann and the correlation is shown in Figure 3.8 using the data in Table 3.6:

Sustituent	δT_8	$\delta T_6/\delta T_8$	δT_6	Calculated δT_6
Octyl	-66.64	0.813025	-54.18	-54.6448
3-Cyanopropyl			-55.46	
Phenyl	-79.7	0.839272	-66.89	-65.354
Benzyl	-70.12	0.8417	-59.62	-57.4984
Cyclohexyl	-68.69	0.823992	-56.6	-56.3258
Cyclopentyl	-66.55	0.81698	-54.37	-54.571
iso-Butyl	-67.9	0.8162	-55.42	-55.678
7-Octenyl			-54.25	
Methylpentanoate	-66.06	0.8571	-56.62	-54.1692
3-p-methoxyphenylpropyl	-66.77	0.815037	-54.42	-54.7514

Table 3.6 – Estimated T_6 chemical shift.

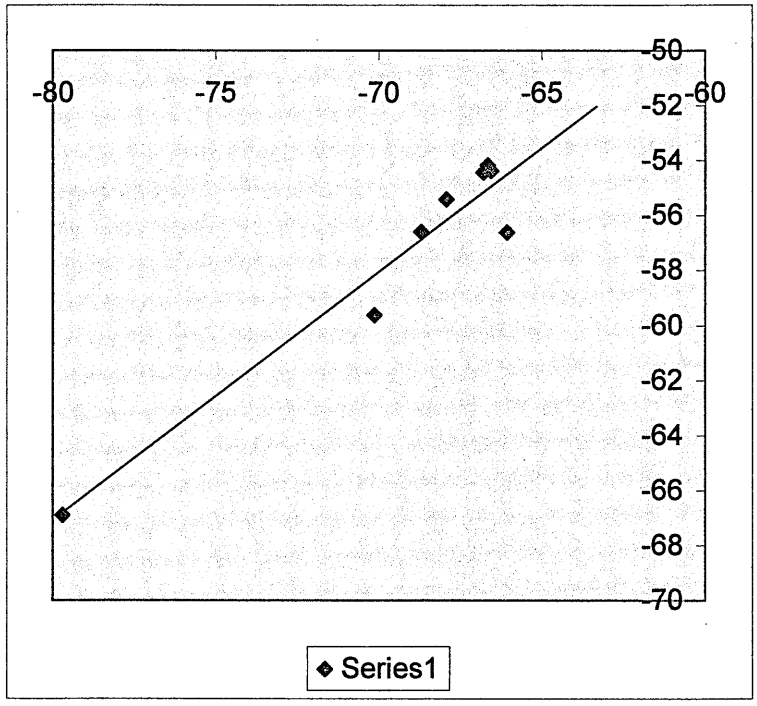


Figure 3.8 – Correlation of chemical shift.

Figure 3.8 has a slope of 0.82 if forced to go through the origin ($R^2 = 0.92$), thus the equation for δT_6 will be:

$$\delta T_6 = 0.82\ \delta T_8$$

Using this equation the last column in Table 3.5 is easily calculated. Apart from one or two exceptions the difference between the observed and calculated chemical shifts is relatively small confirming this type of correlation is equally valid for T_6 cages as for T_{10} and T_{12} cages.

3.10 – Conclusion.

In the previous chapter the synthesis of D_n rings via "non-aqueous" hydrolysis of dichlorosilanes was discussed. We reported that D_3 is the preferred product when

dichlorosilanes are treated with oxygen donor compound but interconversion into larger rings occurs because of the ring strain energy of such molecules.

Based on the same criteria we expected that "non-aqueous" hydrolysis of trichlorosilanes could lead to T_3 as the initial product which then may be converted into T_8 and/or bigger cages. T_6 cages have been isolated by ordinary hydrolysis but only with cyclopentyl and cyclohexyl groups as substituents.

Treating trichlorosilanes with the oxygen donor compounds used in chapter 2 we proved that only DMSO gave a reasonable amount of products and, surprisingly, in several cases we were able to isolate stable T_6 compounds. The trichlorosilanes were chosen with different R groups. We demonstrated that if the substituent on the silicon is reasonably large it might act as templating agent in the ring formation which may be the precursor of the cage. As D_3 is the preferred ring in the non-aqueous hydrolysis of dichlorosilanes in the same way T_6 is the preferred cage as result of the bond between two D_3 rings.

Small R groups in the starting trichlorosilanes did not lead to cages but they gave formation of resins. The same result was obtained when trichlorosilanes carrying linear chains as substituent were used, with the exception of octyltrichlorosilane..

More interestingly, the results obtained with cyclopentyl- and cyclohexyltrichlorosilane, octyltrichlorosilane, *iso*-Butyltrichlorosilane, Methyl 3,3-dimethyl-5-trichlorosilylpentanoatetri-chlorosilane and 3-(*4*-Methoxyphenyl)propyltrichlorosilane gave the corresponding T_6 compounds in yields sufficiently high to be isolated in some cases.

Octyl-, *iso*-Butyl-T_6, Methyl 3,3-dimethyl-5-trichlorosilylpentanoate-T_6 and 3-(*4*-Methoxyphenyl)propyl- T_6 were synthesised for the first time but only the last one was crystalline and it was possible to characterise it by crystal structure.

The result obtained with phenyltrichlorosilane was also interesting: the resonance in the ^{29}Si-NMR suggested the presence of the corresponding T_6 but all the attempts to isolate the pure product failed, giving a resin.

CHAPTER 4

SYNTHESIS OF

LINEAR AND CYCLIC POLYOLS

4.1 – Introduction.

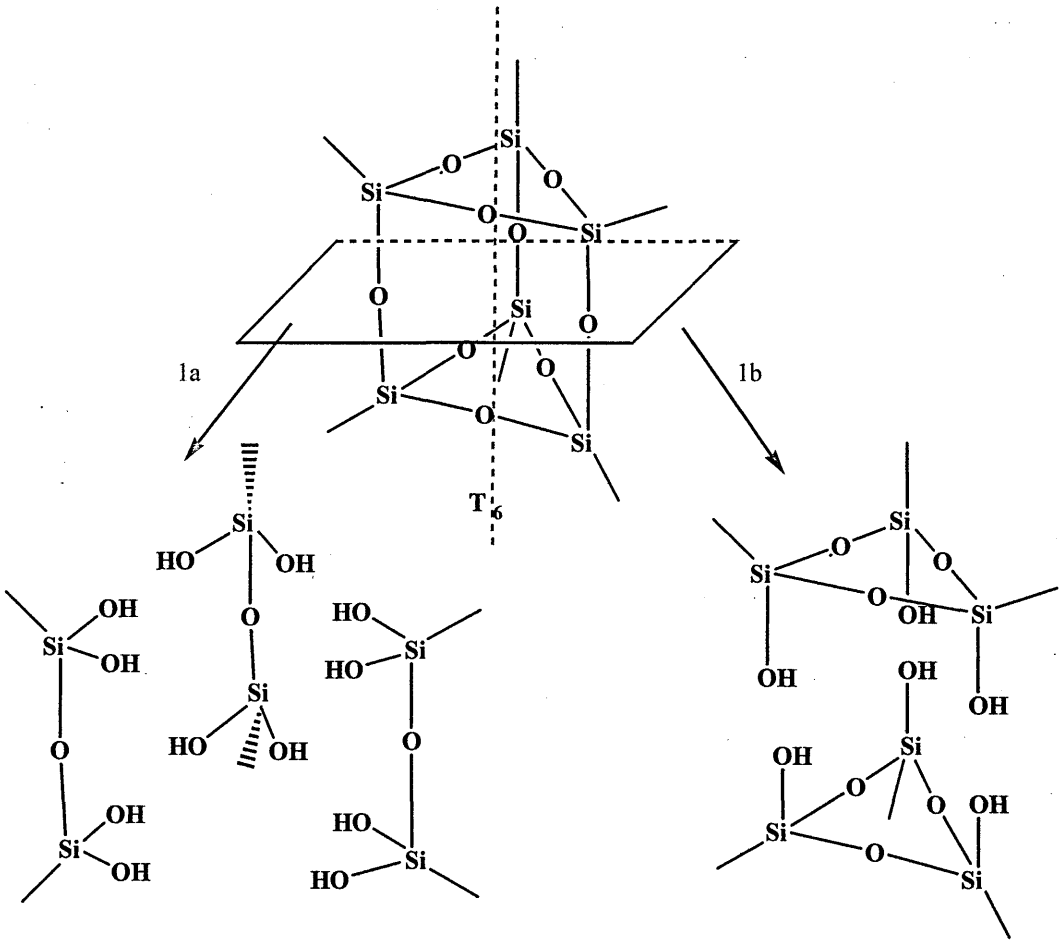
Previously, in Chapter 2, we described the hydrolysis of dichlorosilanes and discussed how such hydrolysis gave, as major products, D rings. We also demonstrated that, under certain conditions, and using the reagent DMSO, it is possible to improve the yield of the smallest ring of the series, D_3.

In Chapter 3 we discussed how the "non-aqueous" hydrolysis of trichlorosilanes leads preferentially to T_6 cages, whereas the ordinary hydrolysis with water leads to T_8 cages. We have further described how the structures of some of these T_6 and T_8 cages have been confirmed using X-Ray crystallography.

The "non-aqueous" hydrolysis represents an effective method of synthesis of T_6 in reasonable yields and, for certain T_6 cages, it represents the only method of preparing them. We wish to improve the yield of such cages, and thus this chapter discusses a different approach to the synthesis of T cages based on an analysis of their three dimensional structure.

Retrosynthetic analyses of T_6 or T_8 cages are shown in Schemes 4.1 and 4.2.

T_6 and T_8 are three-dimensional highly symmetric molecules and therefore they have axes and planes of symmetry. Obviously, since the geometry of the two types of molecule is not the same, the planes and axes of symmetry are different in the two cages. The T_6 cage has a prismatic shaped core while the T_8 molecule is cubic. A prism has a three-fold rotation axis and a plane of symmetry perpendicular to that axis, cutting the molecule into two identical parts, two D_3 rings (Scheme 4.1 arrow 1b). In the same way a T_8 cage has a four-fold rotation axis and a plane perpendicular

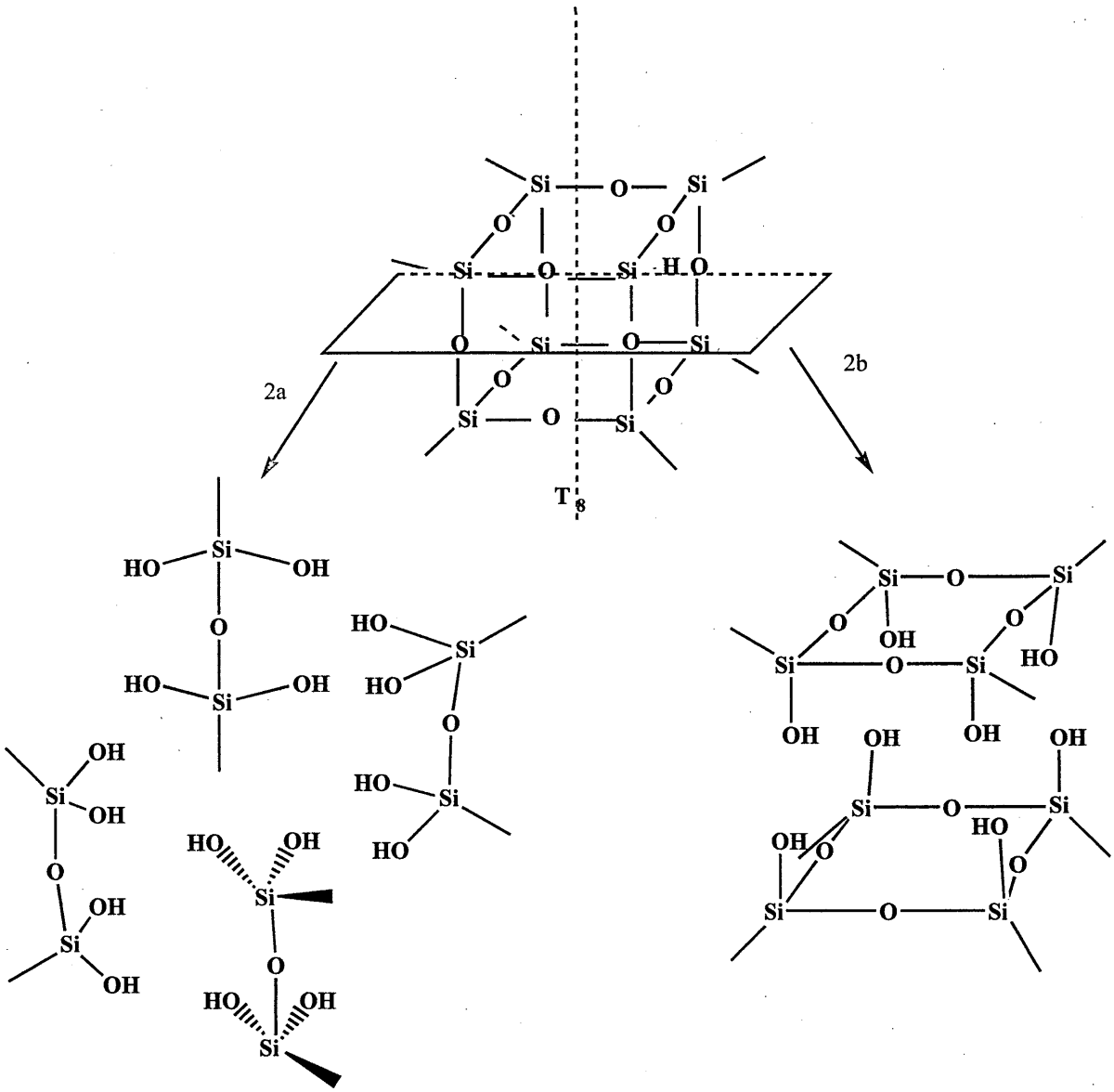


Scheme 4.1 – Rettrosynthetic analysis of T_6

to that axis that divides the cage into two D_4 rings (Scheme 4.2 arrow 2b).

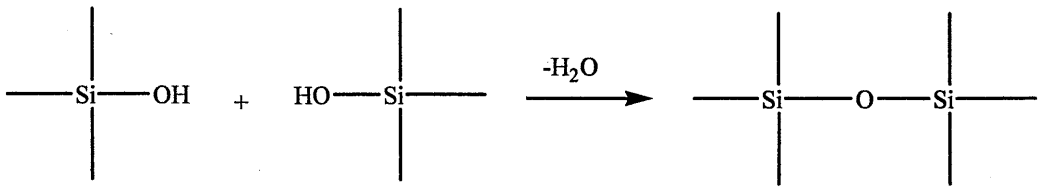
A further approach is to consider the bonds that form the corners of the cages. For T_6 and T_8 the corners disconnect to give three or four disiloxane molecules, respectively (Scheme 4.1 arrow 1a and Scheme 4.2 arrow 2a).

In Schemes 4.1 and 4.2, the OH group has been identified as the reactive substituent because the easiest way to synthesise such cages is from the triol/tetrol, either as a



Scheme 4.2 – Retrosynthetic analysis of T_8

ring or as a disiloxane. This is because a siloxane bond, is readily formed by the condensation of two Si-OH groups with the associated loss of water, as shown in the Scheme 4.3.



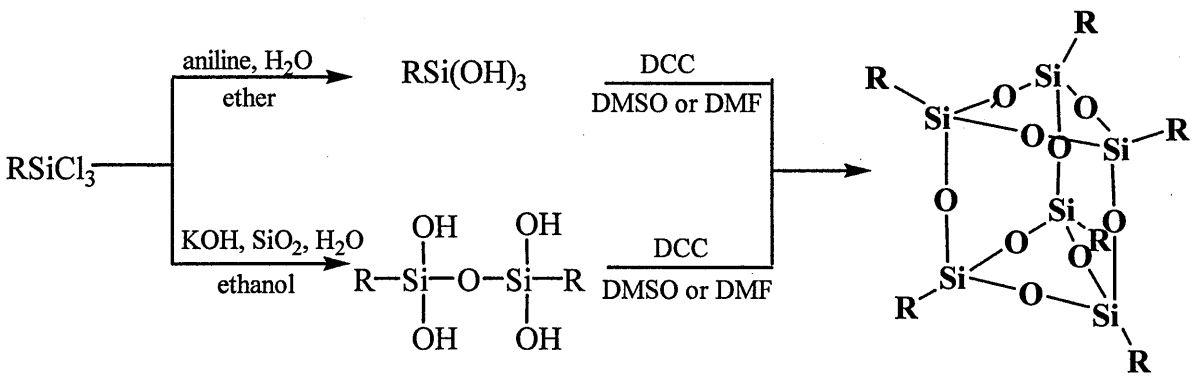
Scheme 4.3 – Siloxane bond formation.

Following this approach, the synthesis of T_6 and T_8, can be broken down into two steps:

1. The synthesis of the corresponding disiloxanetetraol or the cyclic triol or tetrol.

2. The coupling of the previously synthesised polyol molecules.

Unno and co-workers[186] have reported a method for the synthesis of a series of disiloxanetetrols using trichlorosilanes as starting material, carrying a bulky group such as thexyl (1,1,2-trimethylpropyl) and *tert*-butyl. According to Unno's paper, the treatment of the trichlorosilanes with aniline and water in ether leads to the corresponding silanetriol that can be coupled to form the disiloxane tetraol. When the trichlorosilane is treated with KOH in the presence of SiO_2 and H_2O in ethanol, the reaction product is the corresponding disiloxane tetraol with no further reaction. A subsequent treatment with a dehydrating agent such as DCC (dicyclohexylcarbodiimide) in DMSO or DMF leads to the formation of the T_6 cage.



R=thexyl, *tert*-butyl **Scheme 4.4** – Unno reaction for the T_6 synthesis.

Based on Unno's strategy for the synthesis of T_6 cages we used different trichlorosilanes to obtain disiloxanes with a range of functionalities attached to the silicon atom. The trichlorosilanes used included the cyclohexyl and the *tert*-butyl group, thus repeating Unno's procedure and enabling us to characterise the *tert*-butylhexasilsesquioxane.

4.2 – T_6 via condensation of disiloxanetetrol.

According to Schemes 4.1 and 4.2 one method of synthesising functionalised T_6 and/or T_8 cages is via the corresponding linear disiloxanetetraol. We repeated Unno's procedure for the condensation of the linear disiloxanes, but used a different procedure to synthesise the disiloxane, which was provided by Dow Corning (see note on page 47).

This synthesis involved a hydrolysis/condensation of a trichlorosilane using water and MIBK(3-methylpentan-2-one). The trichlorosilane was added dropwise to the two phase mixture and the disiloxane precipitated almost immediately; however, the mixture was stirred for a further period of 24 h in order to increase the yield.

4.2.1 – Results and discussion.

Using the Dow Corning procedure linear disiloxanes have been successfully synthesised using cyclohexyl- and 5-(bicycloheptenyl)trichlorosilanes as well as *tert*-butyltrichlorosilane, Table 4.1 lists all the attempted syntheses of the disiloxanetetraol with the general formula shown in Figure 4.1

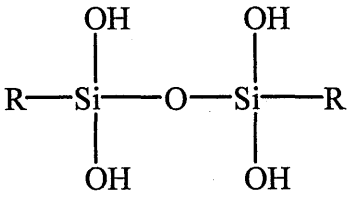


Figure 4.1 – General formula of disiloxanetetraol.

Starting trichlorosilane	Success
cyclohexyltrichlorosilane	Yes
5-(bicycloheptenyl)trichlorosilane	Yes
tert-butyltrichlorosilane	Yes
vinyltrichlorosilane	No
7-octenyltrichlorosilane	No
octyltrichlorosilane	No
3-(4-methoxyphenyl)propyltrichlorosilane	No

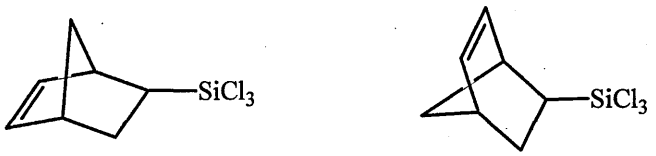
Table 4.1 – Trichlorosilanes used in the synthesis of the corresponding disiloxane and their success.

The ^{29}Si-NMR of cyclohexyldisiloxanetetraol gave a resonance at -51.2 ppm and the *tert*-butyldisiloxanetetraol gave a resonance at –49.6 ppm. The ^{29}Si-NMR of the product obtained using bicyclotrichlorosilane was a little more complicated: the spectrum shows a major peak with a chemical shift of –52.1 ppm plus other smaller peaks at –50.5 ppm, -50.9 ppm and –51.1 ppm. As it was not possible to identify these products by simple NMR analysis, it was decide to analyse the disiloxanes by mass spectrometry.

The mass spectrum shows two major peaks the first one at m/z=358 and the second at m/z=344 with an intensity of 100%. The peak with the lower molecular weight

represents the disiloxane plus NH_4^+ which is used to ionise the sample. The peak at m/z=358 had an intensity of about 25% and is probably due to an impurity in the starting material itself.

The starting material is in reality a mixture of two isomers, as shown in Figure 4.3



A B

Figure 4.3 – Possible isomers of starting material

of which the predominant form is probably B. The coupling of this mixture of two isomeric trichlorosilanes to give a disiloxane takes place to give a number of isomers; for example, the dimer B—O—B might be attributable to the resonance at –52.1 ppm (based on intensity), while with A—O—A in Figure 4.4 and A—O—B would account for the presence of three other resonances.

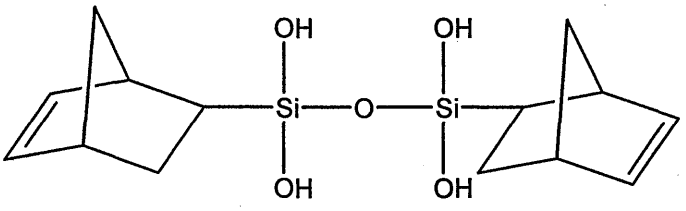


Figure 4.4 – One of the possible structures of the bis-(5-(bicycloheptenyl))disiloxanetetraol.

We carried out the Dow Corning procedure for the synthesis of disiloxanetetraols with several trichlorosilanes with different functionalities. Only trichlorosilanes with reasonably bulky groups, as listed in Table 4.1, gave satisfactory results. For example, with linear trichlorosilanes such as octyltrichlorosilane, 7-octenyltrichlorosilane and

3-(4-methoxyphenyl)propyltrichlorosilane, the reaction gave a broad resonance in the ^{29}Si-NMR, characteristic of a resin. Nevertheless the resonance were in the region for the chemical shift expected for a disiloxane (-49 and –51 ppm). A possible reason why trichlorosilanes with smaller groups do not give disiloxanes comes from an analysis of the crystal structure shown in Figure 4.7.

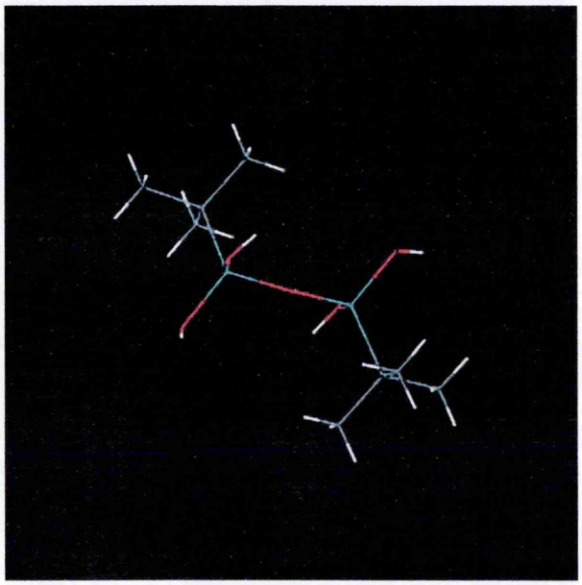


Figure 4.7 – X-Ray crystal structure of *tert*-butyldisiloxanetetraol.

Whilst this structure was obtained in this study, the structure of the *tert*-butyldisiloxane, as well as related data, were published by Lickiss in 1995[199]. As Lickiss reported in his paper, in a disiloxane molecule containing a bulky substituent like *tert*-butyl, the hydrogen bonds between the –OH groups can no longer occur intramolecularly because of their relative positions in keeping the two bulky *tert*-butyl groups as far apart as possible. In fact, *tert*-butyldisiloxane forms strong intermolecular hydrogen bonds. The X-ray crystal structure that we obtained is not very different from that obtained by Lickiss. The major difference arises from the Si—O—Si angle: in Lickiss' structure, this angle is 171.6° whereas in our structure the same angle is 166.5°. However, this difference is not surprising because the flexibility

of the Si—O—Si angle is well known in these types of molecule and the difference could be attributed to slightly different packing and thus different intermolecular hydrogen bonding.

4.2.2 – Condensation of cyclohexyldisiloxanetetraol.

As reported in Unno's paper, condensation via the dehydration of *tert*-butyldisiloxanetetraol leads to the corresponding T_6. We repeated this procedure using cyclohexyldisiloxanetetraol but obtained a different product. The ^{29}Si-NMR of the crude mixture obtained following the Unno procedure showed no trace of the starting material, but unfortunately it was not possible to distinguish any sharp resonances in the T_6 or T_8 region. However, a forest of resonances was obtained characteristic of a resin.

The solvent in the Unno procedure was DMSO which, as discussed in the previous Chapters, is a possible source of oxygen and therefore can undergo nucleophilic attack on the silicon in the disiloxane. As a result of this the disiloxane may have undergone a rearrangement, leading to a resin. To avoid this, an alternative solvent was chosen which would have good solubility for the starting material and also not give rise to other reactions. We thus tried THF; however, the reaction between the cyclohexyldisiloxanetetraol and DCC still did not give the expected T_6 or T_8.

DCC is a dehydrating agent that, once reacted, forms a urea that is very difficult to remove from the reaction mixture it is partially soluble in THF, and therefore, initially it can be removed by filtration. However, on evaporation of the solvent it further crystallises out making it difficult to separate and purify the products.

We thus decided to use a different dehydrating agent and chose Martin's sulfurane Figure 4.5.

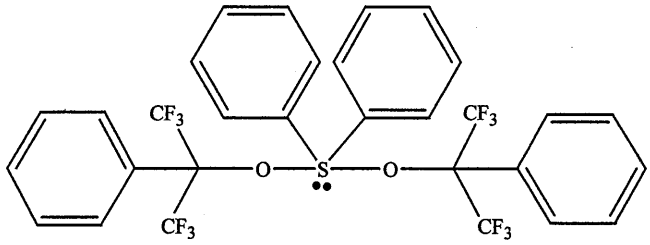
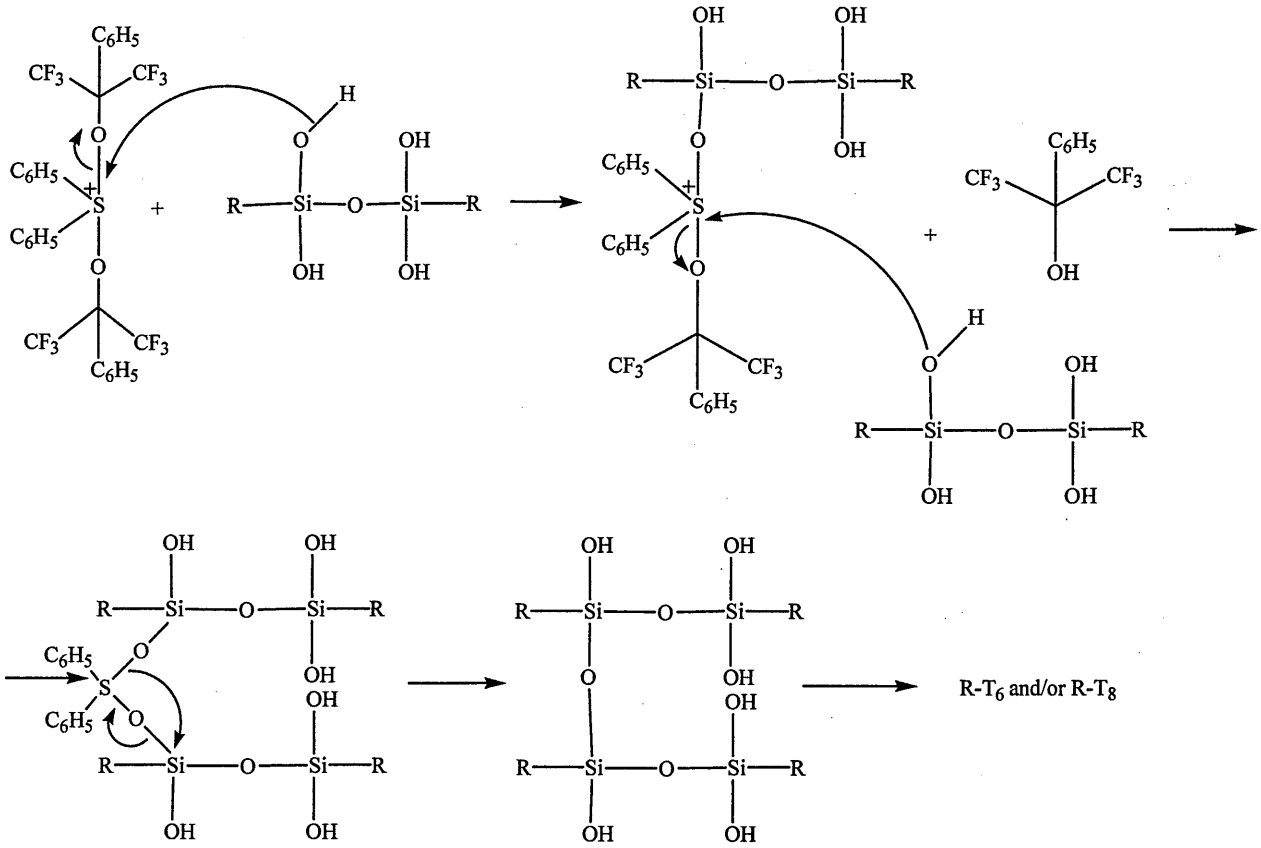


Figure 4.5 – The structure of the Martin's sulfurane.

Martin's sulfurane has been known as a dehydrating agent since the early 1970. It has been used as a dehydrating agent for secondary and tertiary carbinols giving, under mild conditions, the corresponding olefins.

Using a silanol, the OH group attacks the electrophilic sulfur of Martin's sulfurane (Scheme 4.5).



Scheme 4.5 – Mechanism of thenucleophilic attack of Martin's sulfurane.

The reaction using Martin's sulfurane was performed in THF and the mixture was stirred overnight, after which a ^{29}Si-NMR of the crude reaction mixture was recorded. The spectrum showed a resonance with a chemical shift of –68.5 ppm. This chemical shift is characteristic of T_8 cages and, since cyclohexyl-T_8 had been previously fully characterised, the ^{29}Si-NMR of the solution containing the sample obtained from the reaction was compared with a standard sample of cyclohexyl-T_8. Both gave identical resonancs with the same chemical shift, confirming the presence of cyclohexyl-T_8.

As discussed in Chapter 3, whilst the nature of the oxygen donor compound used in the synthesis of the T_6 is significant, the size of the substituent on the silicon plays the most important role in determining the outcome of the reaction. With the "non-aqueous" hydrolysis methodology, the *tert*-butyltrichlorosilane did not give the corresponding T_6 even though it was obtained using the Unno procedure. The "non-aqueous" hydrolysis did however give the cyclohexyl-T_6. The mechanism hypothesised for the DMSO procedure was via a *cis*-trichlorocyclotrisiloxane intermediate and it may be that the cyclohexyl D_3 is formed more readily than the *tert*-butyl D_3. In the Unno procedure the starting material is the disiloxane which has the structure shown in Figure 4.6

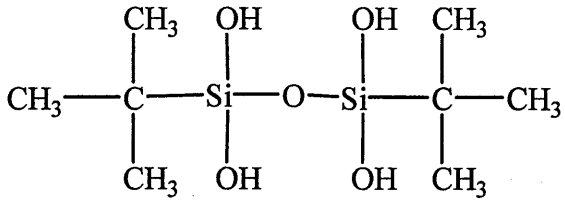
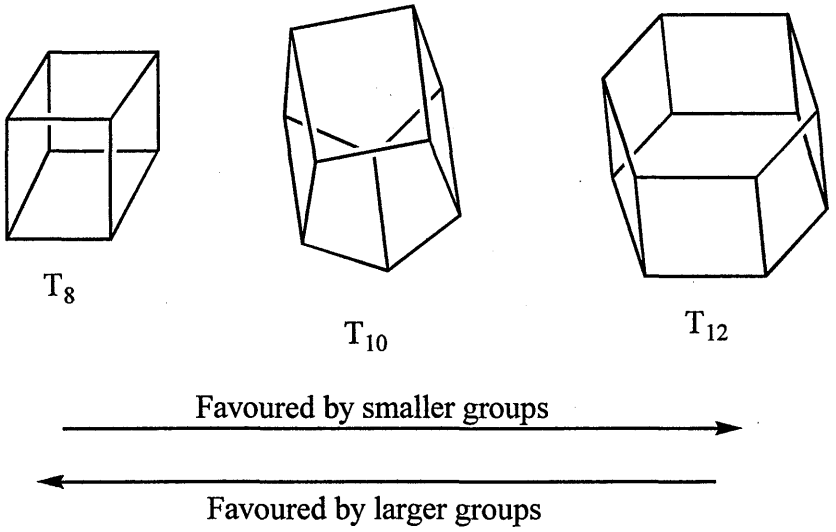


Figure 4.6 –The structure of *tert*-butyldisiloxanetetraol.

We believe it is the steric bulk of the substituent that causes the *tert*-butyl derivative to give the T_6 cage whereas the cyclohexyl compound gives the T_8 cage.

Liu[205] has shown that the reaction of $R'Si(OR)_3$ with tetrabutylammonium fluoride gives silsesquioxane cages where the size of the cage depends upon the size of the R group. Small R groups lead to T_{10} or T_{12} cages whereas medium size groups, such as cyclohexyl, favour T_8 cage formation. Thus, we might expect bulky groups such as those used by Unno to form T_6 cages.



Condensation of the disiloxanetetraol will lead to ladder formations of the type shown on Figure 4.7:

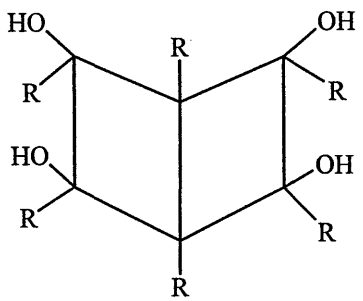


Figure 4.7

When R is bulky the angle between the plane of the two T_4 rings will be smaller, such that the remaining OH groups will be close enough to react to give a T_6 cage. If the R group is smaller the OH groups are not close enough to react and require a further disiloxane tetraol unit to add before the OH groups are close enough to each other as shown in figure 4.8:

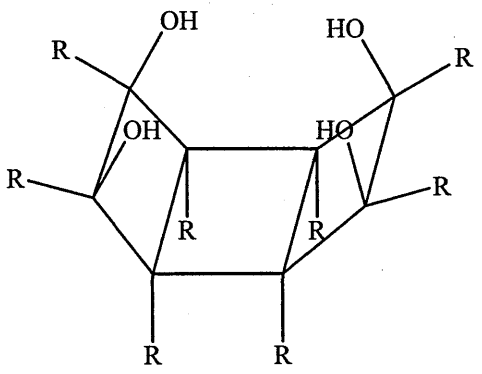


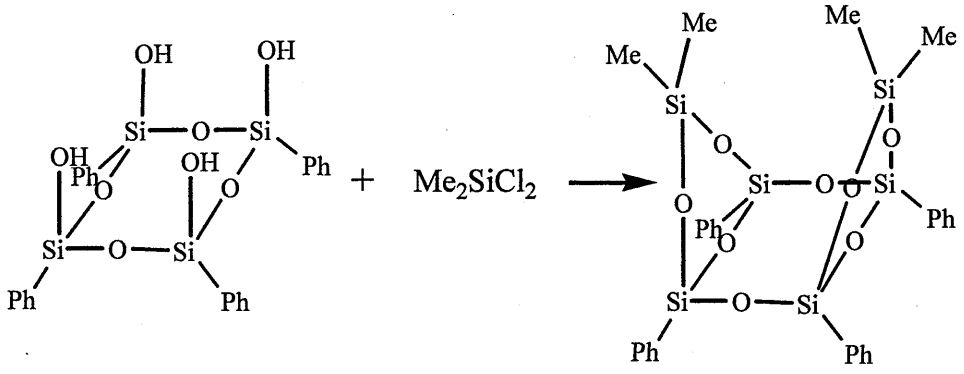
Figure 4.8

In this case, reaction of the adjacent OH groups gives the T_8 cage.

4.4 – T_6 and T_8 via condensation of *cis*-cyclosiloxanetriols and tetraols.

4.4.1 – The synthesis of the *cis*-phenyltetraol: a review of the literature.

1,3,5,7-*cis*-Tetrahydroxytetraphenylcyclotetrasiloxane (referred to as *cis*-phenyltetraol from now on) has been known since 1965 when Brown[184] synthesised it by hydrolysis of the corresponding trichlorosilane in a mixture of water and acetone. The *cis*-phenyltetraol was the main product mentioned in this paper although other side products were obtained such as partially condensed cages, ladders and resins. The paper reports a yield of about 50% of the tetraol and it was identified by reaction with dimethyldichlorosilane which gave the *cis-syn-cis*-tricyclo[7.3.1.1]hexasiloxane (Scheme 4.7), previously characterised by Adrianov[200] and co-workers in 1956.



Scheme 4.7 – The formation of *cis-syn-cis*-tricyclo[7.3.1.1]hexasiloxane.

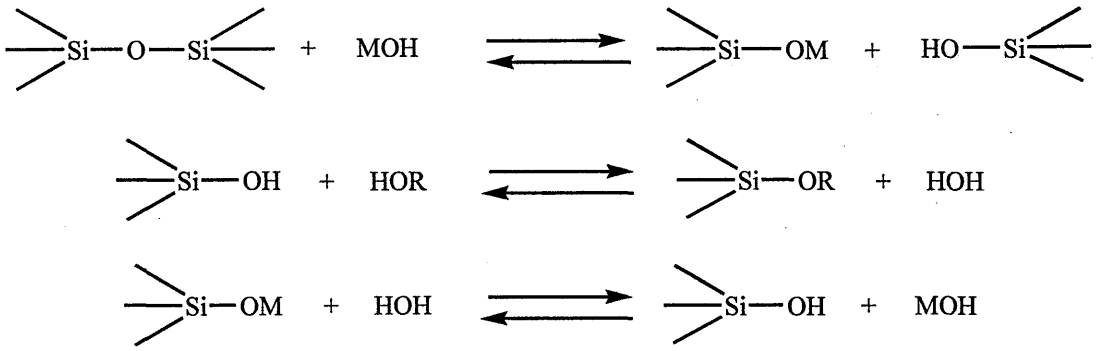
The tetraol was prepared by Brown by washing the crude mixture of the resinous product with carbon disulfide to give a white powder that was too unstable for recrystallization from warm solutions. No further characterisation data was reported at that time apart from a melting point (166-174 °C with decomposition) and the elemental analysis.

The complete series of the four phenyltetraol isomers was obtained by Klement'ev and co-workers[202] by rearranging the product obtained via the Brown procedure using trimethylchlorosilane, dimethyldichlorosilane or HCl. The results were reported in the Russian literature in 1981. The four isomers obtained were separated by TLC and, again, the structure of the isomers, including the *cis* isomer, were identified from analysis of the structure of the products obtained by their reaction with dimethyldichlorosilane and α,ω-dichlorotetramethyldisiloxane. Apart from the melting points, no other physical data was reported in this paper.

In 2000, Shchegolikhina and co-workers[201] published a paper which proposed a different approach to the synthesis of the *cis*-phenyltetrol. A previous paper by Shchegolikhina, published in 1998, had reported a method of synthesising large cage-like metallasiloxanes using an oligoorganosilsesquioxane resin in *n*-butanol.[206] Although the mechanism of this reaction is not yet fully understood, it is thought to

proceed via the formation of $[RSiOONa]_n$. She suggests in her paper, that this intermediate exists, associated with the solvent according to the equilibria shown in Scheme 4.8.

The paper suggests that the reaction occurs in a very similar fashion to that proposed for ordinary aqueous hydrolysis but involves alkaline hydroxide instead of water:



Scheme 4.8 – Scheme of hydrolysis of disiloxane.

The crystal structure of the large rings obtained using this procedure, when reacted with transition metal ions, show a cage type structure consisting of two rings facing each other with the transition metal encapsulated between the rings as shown for a D_8 ring in Figure 4.9

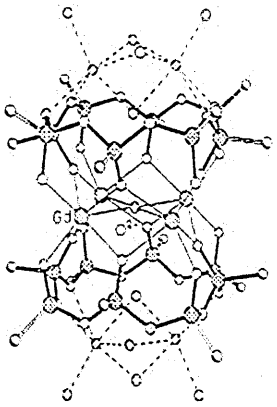


Figure 4.9 – Molecular structure of the complex D_8-transition metal

$(Na_6\{[C_6H_5SiO_2)8]_2Gd_4(\mu\text{-}O)\}\cdot 10EtOH\cdot 8H_2O$

The paper published in 2000 reports the synthesis of smaller siloxane rings with OH groups bonded to the silicon atom and also the crystal structure of the sodium salt of the *cis*-phenyltetrol. The crystal structure provides evidence that the tetrasiloxane ring is almost planar. The molecular structure includes molecules of the solvent (the *n*-butanol) that lie preferentially on one side of the molecule while the other side is occupied by the phenyl rings. Furthermore, water molecules are encapsulated within the structure itself.

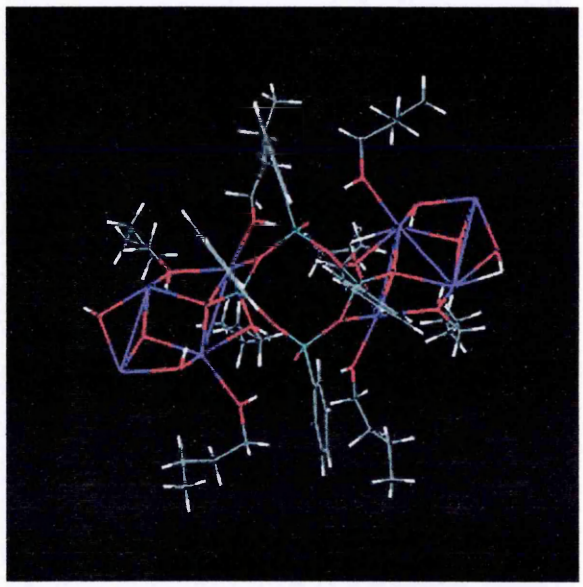


Figure 4.10 - Crystal structure of Shchegolikhina's *cis*-phenyltetrol.

4.4.2 – Our synthesis of *cis*-cyclotetrasiloxanetetraols using the Brown procedure.

An alternative route to synthesise T_6 and T_8 is via the condensation of two molecules of D_3 or D_4 respectively containing OH groups attached to the silicon atoms. As was

shown in Schemes 4.1 and 4.2, one of the requirements for the synthesis of cages from cyclic polyols is that the latter need to have all the OH groups on the same side. The synthesis of both the all *cis*-triol and all *cis*-tetraol is not straightforward. As discussed in Chapter 2, if a silicon atom contains two different substituents, the synthesis of a cyclic compound, will produce a range of isomers. For example, all the possible isomers for phenylcyclosiloxanetetraol are shown in Figure 4.11. This possibility of forming a range of isomers makes isolation of one specific compound very complicated.

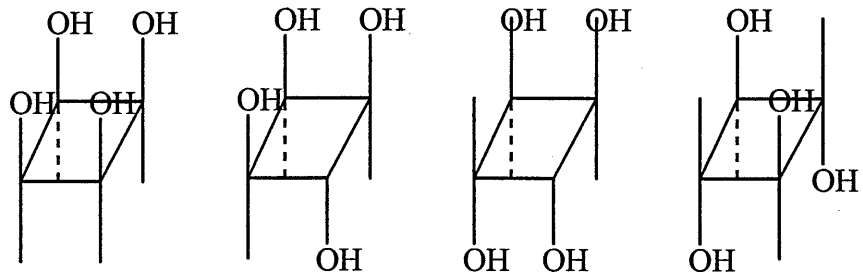


Figure 4.11 – The four possible isomers for the tetraol.

In these representations each corner represents a silicon atom, each side an Si–O–Si bond and the phenyl groups have been omitted. The position of the OH groups with respect to the Phs can be: all four OH groups on the same side (*cis*-tetrol), three OH groups up and one down, two OH groups next to each other up and two down, and two up and two down opposite to each other.

Brown's method of synthesising the all *cis*-tetraol starts from the phenyltrichlorosilane and involves hydrolysis in a mixture of acetone/water. When we repeated this, the trichlorosilane, dissolved in acetone, was added to water very slowly with vigorous stirring at room temperature. After a reaction time of 48 h, a resinous product appeared, together with a solid suspended in the solution. The white powder was separated by filtration and dried in the open air. A ^{29}Si-NMR analysis of the

powder shows a broad resonance in the region of –57 ppm characteristic of a complex resin.

According to Brown's paper, the powder is the *cis*-tetraol. An authentic sample, provided by Dow Corning, containing all the isomers of the phenylcyclo-siloxanetetraol, was analysed by ^{29}Si-NMR. This demonstrated that the resonances arising from the different environments of the silicon in the tetraol isomers lie in the region of about -69 ppm. Figure 4.15 on page 149 shows the chemical shifts of the mixture of isomers. If the disubstituted cyclotetrasiloxane exists as four isomers and the silicon atoms in different environments give separate ^{29}Si-NMR resonances, we should expect six resonances in all. The reason why only five resonances are observed is due probably to the overlap of one or more resonances.

The next problem is to attribute each resonance to the corresponding silicon environment. Thanks to Shchegolikhina, we know that the *cis* resonance comes at -68.95 ppm, and a first estimate at assigning the other resonances can be achieved by considering the ratio of the resonance areas. Phenylcyclotetrasiloxane generates six different silicon environments as indicated in figure 4.12.

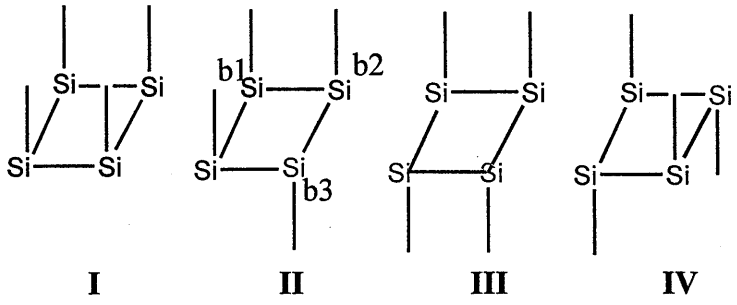


Figure 4.12 - Silicon environments in phenylcyclotetrasiloxane.

The silicon atoms in I are all equivalent, as are the silicon atoms in III and IV. Isomer II contains three different silicon environments b1, b2 and b3, in a ratio 1:2:1.

If we assume that the relative positions of the phenyl groups (i.e. whether they are *cis* or *trans* to each other) has a cumulative effect and this effect is greater the closer the groups are together, we might expect the following order for the ^{29}Si-NMR resonances.

a	all *cis*	68.95 ppm
	(confirmed by Shegolikhina)	
b 1	both neighbours *cis*	
	next nearest *trans*	
b 2	one neighbour *cis*, one neighbour *trans*	
	next nearest *cis*	
c	one neighbour *cis*, one neighbour *trans*	
	next nearest *trans*	
d	both neighbours *trans*	
	next nearest *cis*	
b 3	both neighbours *trans*	
	next nearest *trans*	

Since b 1, b 2 and b 3 should be in a ratio 1:2:1, this suggests that b 1 has a signal at -69.32 ppm and b 3 has a signal at -70.42 ppm. b 2 probably comes at -69.67 ppm which overlaps with c which only differs by the next nearest neighbour. The resonance at -70.06 ppm probably arises from d. This assignment is shown in Figure 4.13.

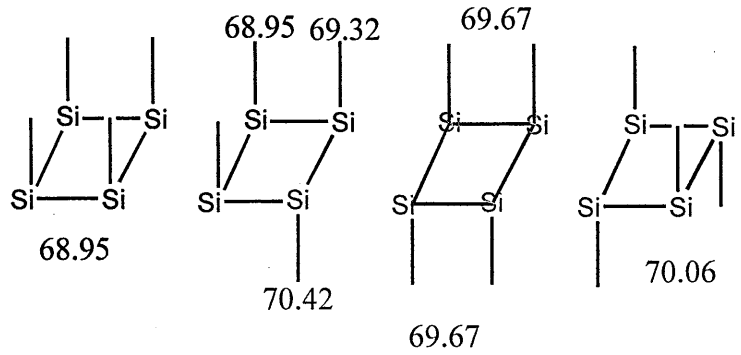


Figure 4.13 – Chemical shifts in phenylcyclotetrasiloxane.

Dow Corning also provided an HPLC analysis of the mixture showing the four peaks corresponding to the four isomers. The HPLC analysis shows the presence of a major component with a retention time of about 13.00 min, which, based on the NMR evidence, is IV. This structure has the phenyl groups as far away from each other as possible and thus, in the absence of other effect, is likely to be formed preferentially. The NMR suggests that b is the next predominant compound (retention time in the HPLC at about 12.1 min) followed by c and a (the peaks with retention time 12.8 min and 13.9 min respectively)

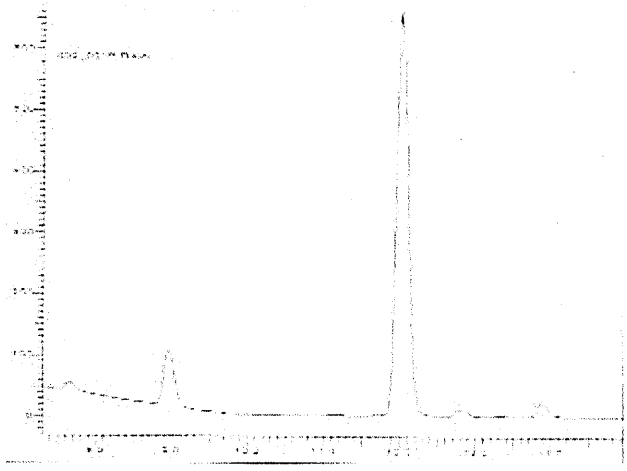


Figure 4.14 – HPLC pattern of a mixture of phenylcyclotetrasiloxane.

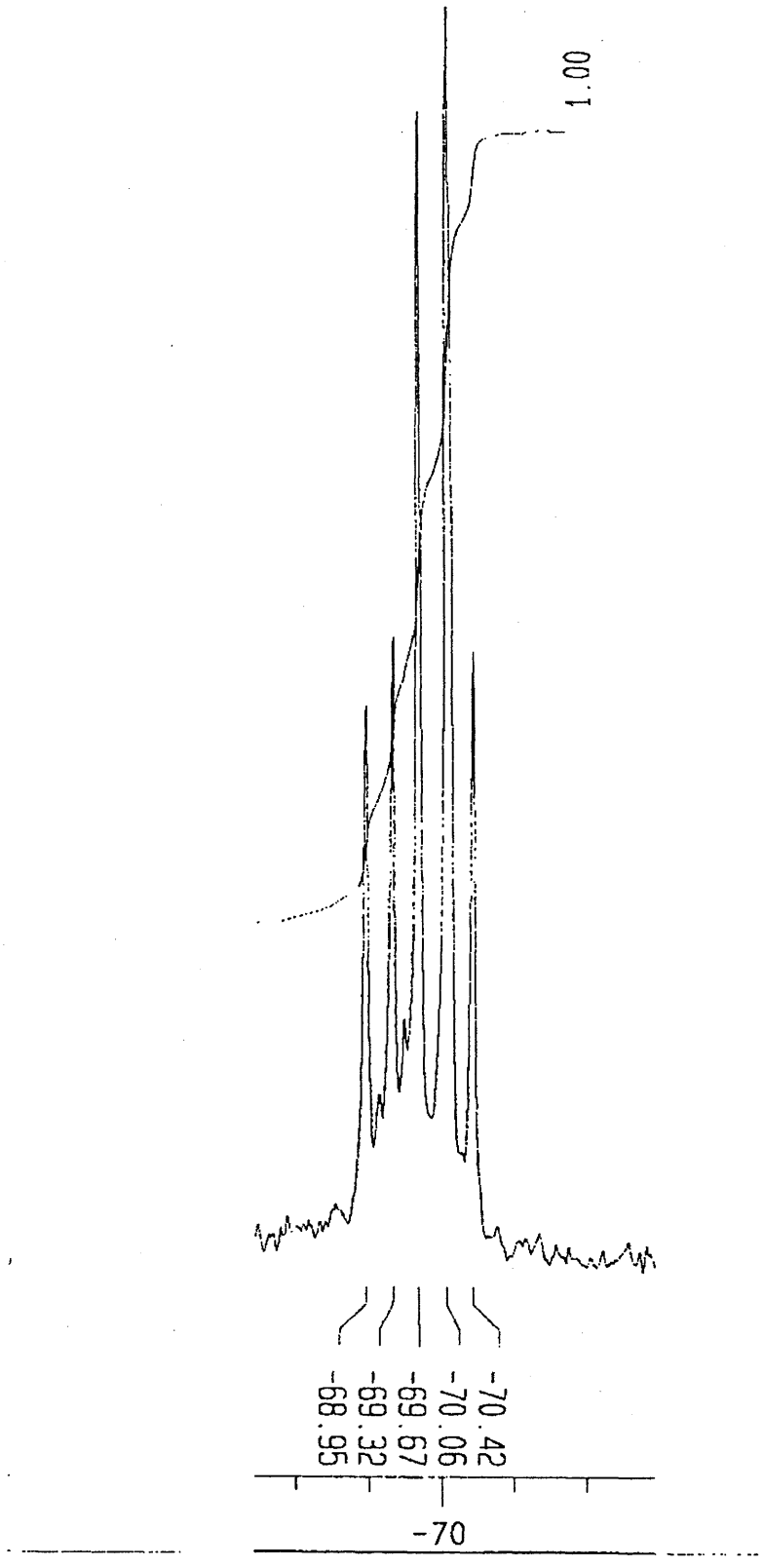
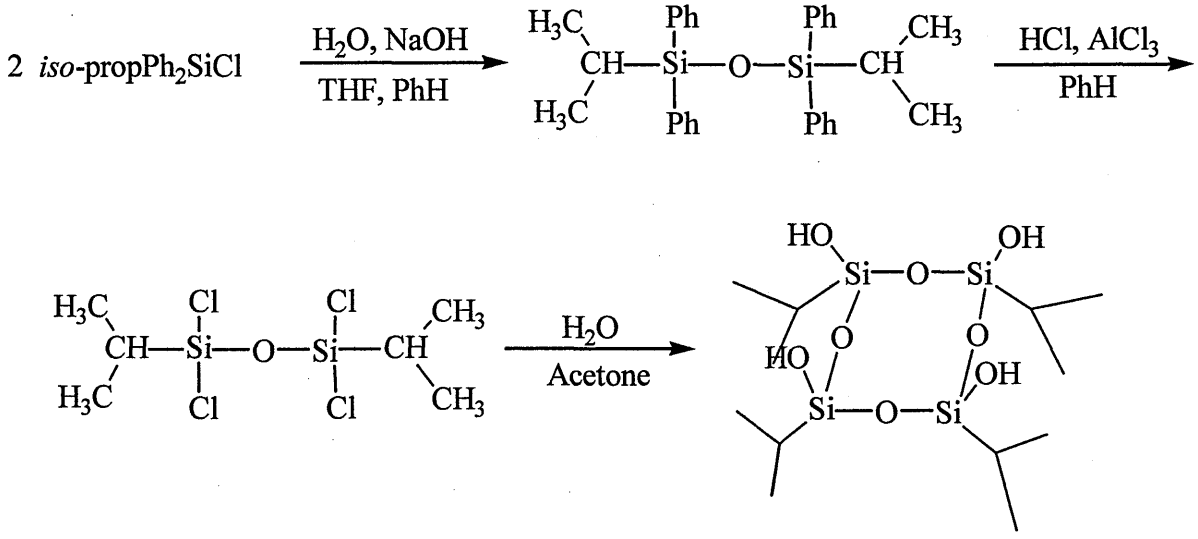


Figure 4.15 - ^{29}Si-NMR pattern of a mixture of phenylcyclotetrasiloxane.

The Brown procedure was repeated several times in our laboratory but we never obtained reasonable samples of the tetraol, only resin.

4.4.3 – The synthesis of cyclotetrasiloxanetetraol. The Unno procedure.

As the method of Brown had not been successful for the synthesis of the tetrol we tried a different approach. In 1996 Unno and co-worker published a procedure for the synthesis of the tetraol via hydrolysis/condensation in water/acetone of tetrachlorodisiloxane. The first step in this procedure was the synthesis of the disiloxane itself. The Unno procedure is summed up in Scheme 4.9:

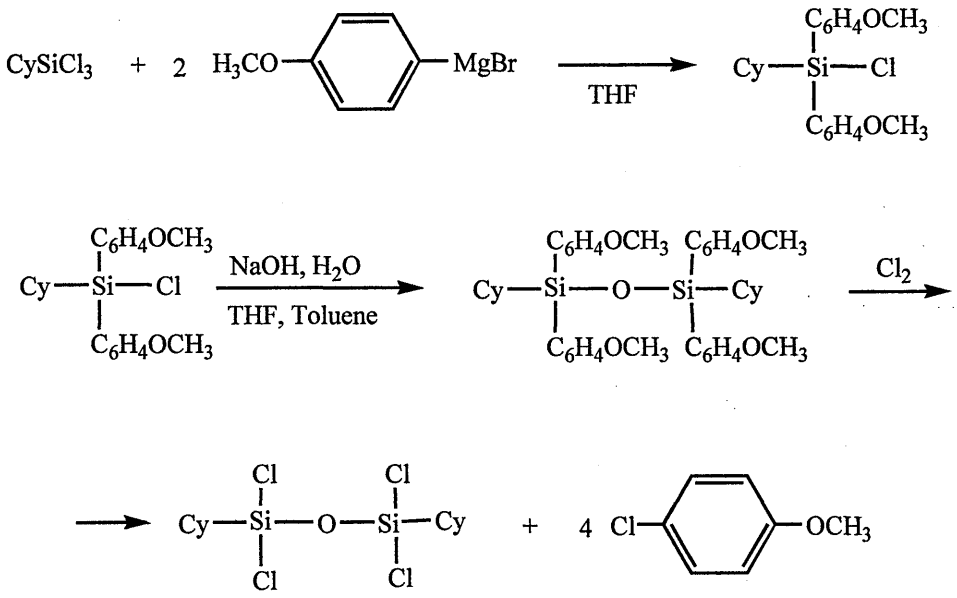


Scheme 4.9 – Synthesis of tetraol via Unno's procedure.

Since the starting material (*iso*-propyldiphenyltrichlorosilane) was not commercially available, we used cyclohexyltrichlorosilane to synthesise the corresponding diphenylchlorosilane. In order to attach the phenyl groups to the silicon atom, a Grignard reagent was used and in particular 4-methoxyphenylmagnesium bromide was chosen, since the methoxy group makes the phenyl ring a better leaving group in

the electrophilic aromatic substitution corresponding to the second step in Unno's strategy.

The following equations show the different steps we employed:



Scheme 4.10

The first intermediate in this reaction is the di(4-methoxyphenyl)-cyclohexylchlorosilane, which, as with all chlorosilanes, is very easily hydrolysed by water present in the atmosphere and was very difficult to handle.

Generally, it is relatively easy to add two equivalents of an organometallic reagent to $RSiCl_3$ but a more reactive organometallic species such as ArLi is required to add a third to form $RSiAr_3$. As we needed to substitute only two chlorines with an aromatic group, a Grignard reagent was chosen.

The reaction was performed by first forming the Grignard reagent and then adding it to the trichlorosilane. It was hoped to separate the product obtained in each step; however, the chlorosilanes and the Grignard proved very difficult to purify. It was then decided to perform the Grignard reaction *in situ*, that is 4-bromoanisole was added to a suspension of magnesium in THF containing the trichlorosilane. Once the

Grignard reaction was complete, a hydrolysis was performed using a base with toluene and THF as solvents. This should have led to the disiloxane intermediate. After 1.5 h gaseous chlorine was bubbled through the solution. A ^{29}Si-NMR spectrum of the product obtained by this route was not satisfactory. The broad peak obtained in the spectrum of the final product was confirmation that this *in situ* reaction leads to a mixture of mono-, di- and probably triarylsubstitution. It was clear that the hydrolysis had given not the expected disiloxane but a polymer having a general formula of $[RSiAr_2O]_n$ and/or $[RSiArO_2]_n$ that was difficult to separate.

Diphenyl-*t*-butylchlorosilane is commercially available and hydrolysis should give the corresponding disiloxane. Unfortunately the hydrolysis, performed using $NaOH/H_2O$ gave only the corresponding silanol. Subsequent coupling using DCC or Martin's sulfurane failed to give the disiloxane. This route was thus abandoned in favour of the more viable route to the tetrol suggested by Shchegolikhina.

4.4.4 – The synthesis of cyclohexyltetrasiloxanetetraol. The Feher's procedure.

More recently Feher[181] has reported an alternative route for the synthesis of a *cis*-tetrol using cyclohexyltrichlorosilane instead of phenyltrichlorosilane. This again used a hydrolytic condensation in acetone/water but this time at reflux temperature. When we repeated this procedure, a cloudy solution was obtained which was filtered and a mixture of solid and resin obtained by washing with acetone. The solid was collected and dried and was shown to have a m.p. of 262 °C, confirming that this was cyclohexyl-T_6. More solid precipitated after washing the mixture of resin in hexane. The first attempt to record a ^{29}Si-NMR of this product failed to give any resonances

and this was presumably due to the poor solubility of the product in chloroform. However accurate mass spectroscopic analysis revealed peaks corresponding to the cyclohexyltetraol and the cyclohexyltetraol plus water, suggesting that the product obtained was the desired tetraol. In the Feher procedure, the product was supposed to be subsequently washed with pyridine but, since we thought that this product was the one we wanted, it was decided not to perform any further purification. However subsequent analysis revealed that the product was something quite different!

In a previous paper, Feher[182] and co-workers published a synthesis of the *cis*-phenyl tetraol based on the Brown's procedure (this time the starting material was phenyltrichlorosilane). The reaction was performed at low temperature, 0 °C, for the addition of the trichlorosilane and maintained at this temperature for a further 5 h. The reaction was subsequently maintained at 5 °C for three days. When we repeated this procedure using cyclohexyltrichlorosilane as the starting material, the solution became cloudy, as indicated by Feher, and, after filtration, we obtained a white solid which should have been the required *cis*-cyclohexylcyclosiloxanetetraol.

According to Feher's paper, the analysis of the resin-like residue gives a wide range of products that have been identified as partially condensed cages and ladders with more than one unit. The same mixture also contains T_6 and T_8 cages. According to this paper, the suspended solid, should have been the *cis*-cyclohexylcyclotetrasiloxanetetrol.

After filtration, the wet solid was analysed by ^{29}Si-NMR and the result is shown in Figure 4.16:

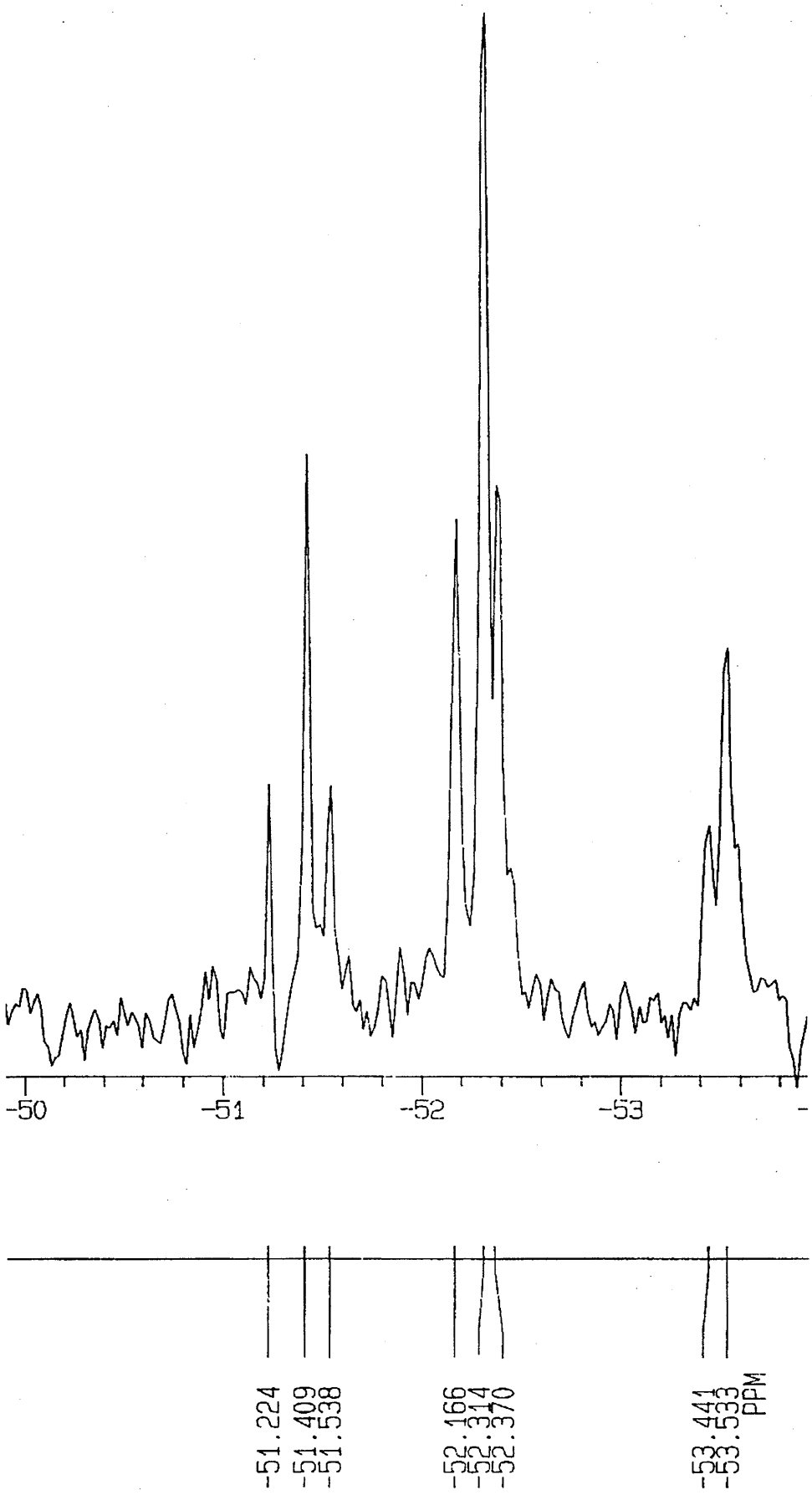
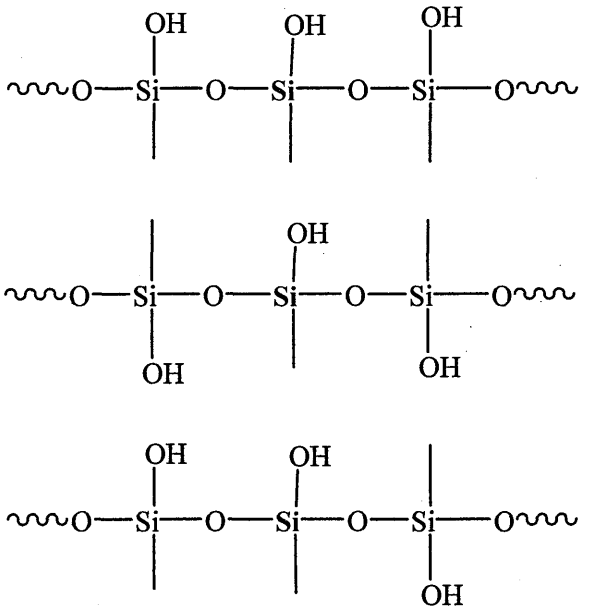


Figure 4.16 - ^{29}Si-NMR of the mixture of polymers.

The triad pattern given by the NMR is characteristic of a linear siloxane polymer. This can be explained by analysing the structure of all the possible arrangements as shown in the Scheme 4.11:



Scheme 4.11

Let us consider the silicon atom marked in red: there are three possible ways for the OH groups to be arranged as indicated in Scheme 4.11:

1. the two OH groups next to the marked silicon can be aligned on the same side;
2. both OH group can be on the opposite side of the OH on the marked silicon one;
3. OH group can be on the same side as the OH on the red silicon and one on the opposite side.

Such an arrangement leads to three signals for the marked silicon with chemical shifts in the region of–51.4 ppm, -52.3 ppm and –53.5 ppm respectively.

If we now consider the silicon atom next but one to the one marked in red and compare the positions of the OH groups with respect to the central Si-OH we again

have the same kind of arrangement; for this reason each of these three signals is again split into a further three resonances.

The wet white powder was dried overnight in the open air and a ^{29}Si-NMR was recorded the following day, (shown in Figure 4.18 on the following page). The spectrumappeared as two sets of two resonances.

The two set of doublets are in agreement with the formation of a linear tetramer for which we can draw two different isomers, Figure 4.17.

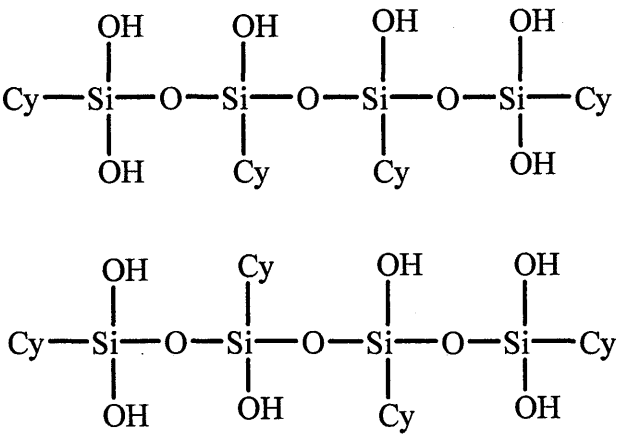


Figure 4.17

The ratio of the peaks (1:1) confirms that the mixture has a 50:50 distribution and therefore there is no preference for either of the two. A MALDI-TOF analysis of the product was also obtained as shown in Figure 4.19 on page 158.

The two peaks indicate the presence of two major products in the mixture. Calculations based on the molecular weight of the polymer confirmed that the peak corresponding to M/z 991 can be attributed to the linear siloxane polymer containing six units $(M+Ag)^+$ and the peak at M/z 703 corresponds to the tetramer $(M+Ag)^+$.

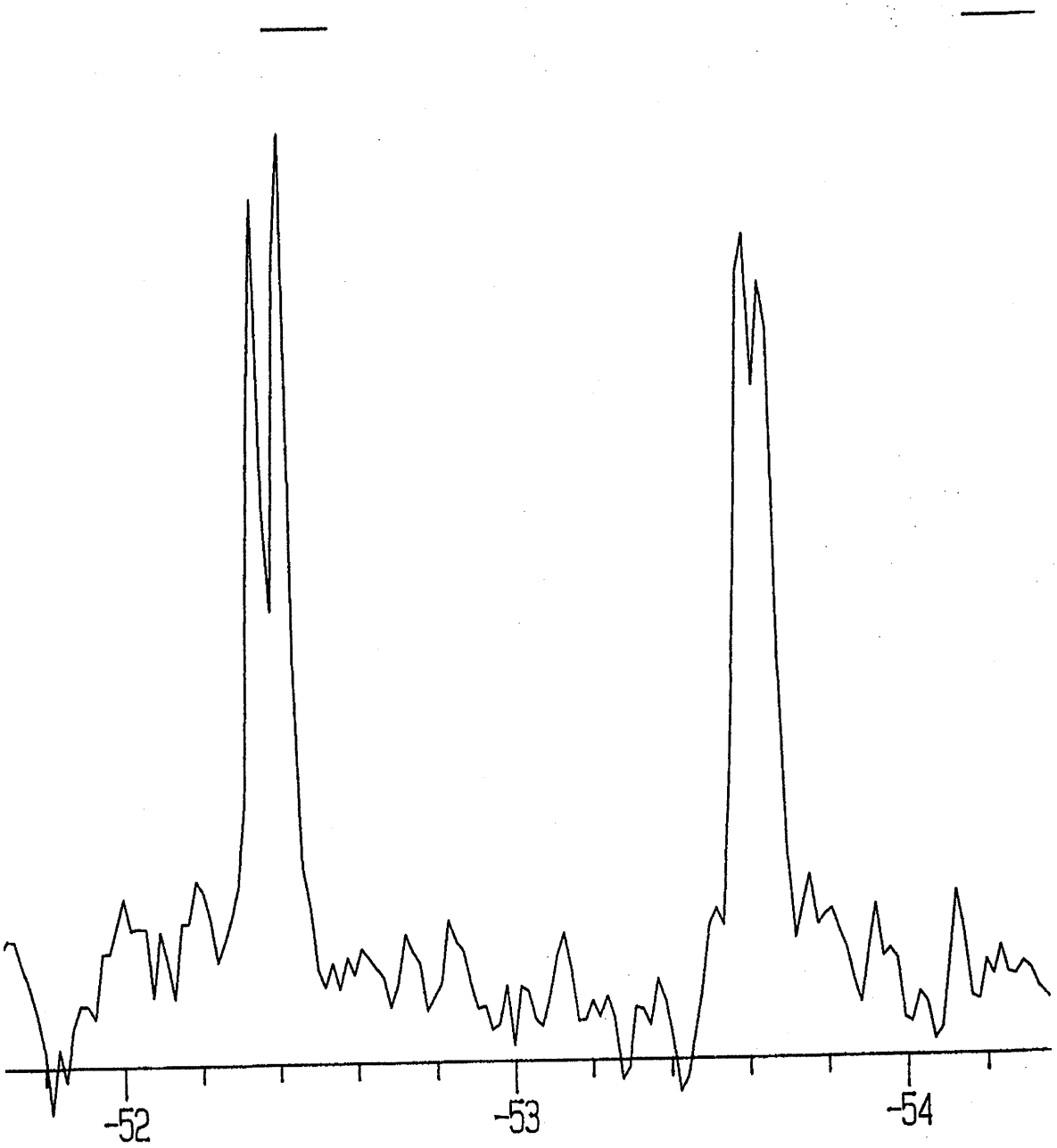
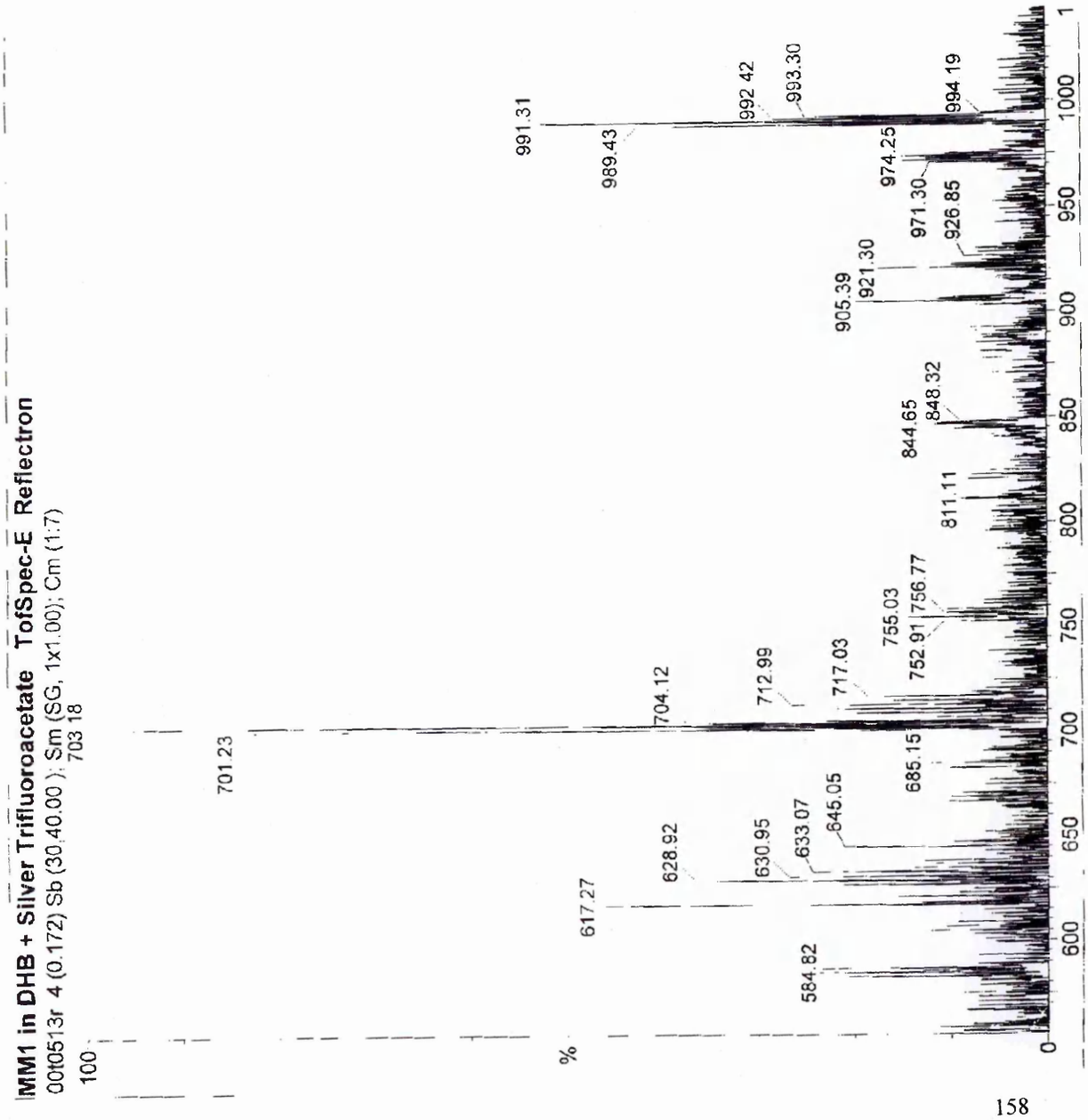


Figure 4.18 - ^{29}Si-NMR after over night drying.

Figure 4.19 – MALDI-TOF of the overnight dried mixture.



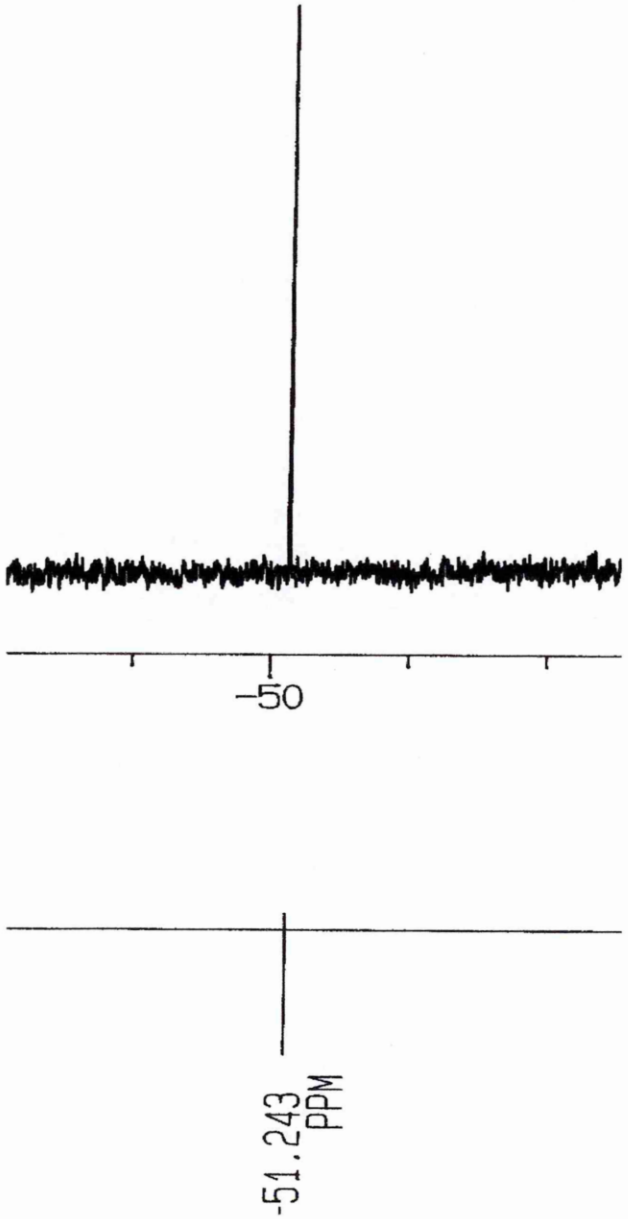


Figure 4.20 - ^{29}Si-NMR of the oven dried mixture of polymers.

The product was placed in the oven at a temperature of 70 °C in order to ensure that the powder was completely dried. After a few hours a further ^{29}Si-NMR spectrum was

recorded. Figure 4.20 shows the spectrum obtained. The single sharp peak at –51.2 ppm was first thought to be due to the desired cyclohexylcyclotetrasiloxanetetraol

In order to monitor the stability of the mixture of phenyl *cis*-tetrols provided by Dow Corning, the ^{29}Si-NMR spectrum of the sample was recorded, from time to time. After several months the NMR spectrum showed that the sample no longer gave the five resonances arising from the different isomers, but gave a single sharp resonance with a chemical shift of –51.9 ppm. We initially thought that the mixture of isomers could undergo, with time, isomerisation giving the most stable tetraol isomer. However, the chemical shift suggests that this is not a tetraol (which has a ^{29}Si-NMR resonance in the region of –70 ppm) but that it had undergone ring cleavage resulting in the formation of the phenyldisiloxanetetraol shown in Figure 4.21

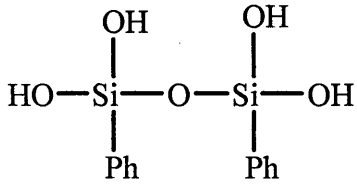


Figure 4.21

Further confirmation of the fact that the product was the disiloxane came from the reaction procedure, provided by Dow Corning*, which was specific for the synthesis of the disiloxane tetraol (see page 110). Reaction of phenyltrichlorosilane with water in MIBK gave a white powder having the same chemical shift (^{29}Si-NMR) as the one obtained over time from the phenyl tetrol mixture. A further confirmation that the white powder provided by Dow Corning was the disiloxane tetraol came from adding some of this powder to the sample obtained by the disiloxane tetraol route. The ^{29}Si-NMR did not show further resonances. Repeating the disiloxane synthesis using

* This procedure has not been published yet by Dow Corning and therefore cannot be reported in this thesis.

cyclohexyltrichlorosilane gave a single resonance in the ^{29}Si-NMR identical to that shown in Figure 4.20. This confirmed that the completely dried product was the cyclohexylcyclodisiloxanetetraol shown in Figure 4.22

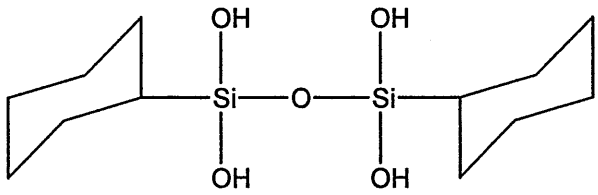


Figure 4.22

4.4.5 – Conclusion.

Both Brown and Feher have reported the synthesis of the *cis*-tetraol. It is possible that the polyol is the actual product formed in the early stage of this hydrolysis, within the first minutes. The polyol subsequently rearranges into more stable molecules, such as partially condensed cages, cages and rings. Nevetherless, over a short time scale we observed no such rearrangement. Our results suggested that the only short term rearrangement of the polymer was the fragmentation of the polymer involving the addition of one molecule of water.

Interestingly the fragmentation never gave a polymer having an odd numbers of units. The polyols observed had respectively six, four and two units. If the fragmentation of the polyol chain occurs randomly, such fragmentation should lead to all possible number of units and therefore polymers with even and odd number of units should be present in the mixture, including the monomer itself, the cyclohexyltrihydroxysilane. The reason why there is no trace of a chain with an odd number of units is not yet clear. We think that one possible explanation could be the importance of forming

intramolecular hydrogen bonds between the OH groups in the chain. When the molecule is wet (first step) hydrogen bonding can occur intramolecularly as well as intermolecularly involving not only hydrogen bonding with other OH groups in the chain but also with molecules of water surrounding the polymer itself. When the polymer is dried there are fewer molecules of water surrounding it. In this case hydrogen bonding only occurs between the OH groups within the same molecule. It may be possible that hydrogen bonding is formed between pairs of monomer units such that subsequent fragmentation leads to even numbers of monomer units in the oligomer.

Since the samples of the polymer were mixtures, it was not possible to obtain a crystal from which we could have obtained an X-Ray analysis confirming its structure. We made several attempts to crystallise the polymer but they were all unsuccessful.

Despite the fact that we did not obtain the expected result, we believe that this outcome is of great importance for our understanding of silicone polymers. A polymer with pendant OH groups leads the way to numerous possibilities. The OH groups could be easily converted into different substituents. Furthermore, the presence of the OH group gives the possibility of forming a cross-linked polymer via dehydration.

4.4.6 – The successful synthesis of *cis*-phenylcyclotetrasiloxanetetraol.

In 2000, Shchegolikhina[201] published a paper which reported a novel method for the synthesis of the *cis*-phenylcyclotetrasiloxanetetraol. Such a two-step method involves the formation of a sodium silanolate. The sodium ions act as a templating agent to form the siloxane ring with the OH groups on one side and the phenyl groups on the

other. This particular disposition of the sodium ions and oxygen atoms forces the ring to crystallise in a cage-like structure.

The synthesis begins with the hydrolysis of the phenyltrichlorosilane to form a resin. This step can be avoided if the corresponding triethoxysilane is employed as the starting material. The resin is subsequently converted into the sodium siloxysilanolate and then, by treatment with excess HCl, the sodium ions are removed and protonation leads to the silanol.

The starting material we used was phenyltriethoxysilane which was dissolved in butan-1-ol. A stoichiometric amount of water and sodium hydroxide (the ratio $PhSi(OEt)_3/H_2O/NaOH$ was 1:1:1) was added, stirred and warmed until the sodium hydroxide was completely dissolved. The temperature was then raised to reflux and the solution stirred for a further half hour.

The solution was left to cool to room temperature and formation of crystals was observed. As Shchegolikhina reported in her paper, the crystals are the sodium salt of phenylcyclotetrasiloxanetetrol. This salt can be stored for only a very short time in the butanol solution (decomposition was observed after two weeks) so it was filtered and dissolved in toluene with sufficient ethanol to dissolve the salt completely (for 10 g of product, 15-20 ml of ethanol were needed). The solution was then added to a large excess of water and hydrochloric acid. The formation of the phenylcyclotetrasiloxane is almost immediate and, after complete addition, the solid was filtered and washed with a large amount of water to remove the HCl residue (acids catalyse the ring opening). We obtained the hydrolysed tetrol in a yield of 65-68% in agreement with Shchegolikhina's paper.

Phenyltetrol is reasonably stable and can be stored for some months before it undergoes ring opening. For this reason it was prepared on a large scale.

We repeated this procedure and obtained a white powder that had a single resonance in the ^{29}Si-NMR with a chemical shift of –59 ppm confirming the presence of a single product with a single Si environment, which was the expected *cis*-phenylcyclotetrasiloxanetetrol.

Following the same procedure we repeated the reaction using a range of trichlorosilanes as the starting materials, in particular we used cyclohexyltrichlorosilane and cyclopentyltrichlorosilane.

Again the trichlorosilane was first converted into the resin and then, by alkaline hydrolysis, converted into the sodium siloxysilanolate.

The sodium siloxysilanolate was analysed by X-Ray diffraction and surprisingly the ring that we had formed turned out to be the three membered siloxane ring rather than the four membered siloxane ring reported by Shchegolikhina, as shown in Figure 4.23.

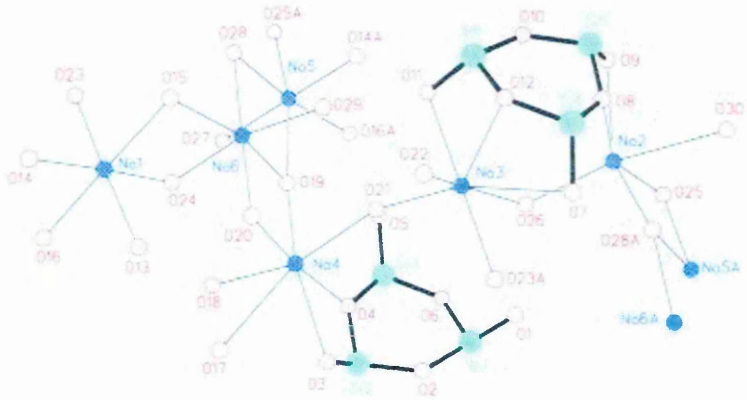


Figure 4.23 - X-Ray diffraction of cyclohexyl sodium siloxysilanolate.

The X-Ray analysis (reported in Appendix on page 253) clearly shows the siloxane ring, with the oxygen atoms located on the same side, complexed to the sodium ions which, again, act as a templating agent for the oxygen atoms. The crystal structure of this product is very different to that of the phenylsiloxysilanolate. As this product was not soluble in chloroform it was not possible to record a ^{29}Si-NMR. The full NMR

analysis was performed on the hydrolysed product (the triol Si-OH rather than the Si-O^-Na^+ formed by treating the anionic form with HCl). This gave a resonance in the ^{29}Si-NMR with a chemical shift of –59.38 ppm. However, this is the region expected cyclohexyl*tetraol* which is anticipated to have a ^{29}Si NMR resonance about 10 ppm downfield from the chemical shift of the corresponding phenyltetraol.

4.4.7 – Comparison between the phenylcyclotetrasiloxanolate and cyclohexylcyclotrisiloxanolate structures.

The sodium phenylcyclotetrasiloxanolate has a cage-like structure (p 140) with the sodium atoms placed between the two rings. With the sodium cyclohexylcyclotrisiloxanolate the two rings are shifted with respect to each other and the whole structure appears to be ladder-like. The rings formed alternate layers with the oxygen atoms pointing in the direction of the sodium ion and the cyclohexyl rings pointing in the opposite direction (complete crystal structure in Figure 6 on page 253). In structures such as the phenylsiloxysilanolate the sodium ion has to be shared between the four oxygen atoms from each ring. As a result the sodium ion is not equally shared between the two opposite rings. The non-symmetric distribution of the sodium ions means that the minimum energy structure for the whole system appears to be a cage-like structure, as described in Shchegolikhina's paper. In our three-membered siloxane ring system, the sodium ion is shared between three oxygen atoms from each ring, resulting in a more symmetric distribution of the sodium ions. This shifts the rings relative to each other and results in an alternating layering of the siloxane rings in the crystal.

Furthermore, in Shchegolikhina's structure, the phenyl groups are not distributed in a symmetrical fashion resulting in a non-perfectly ordered structure. In the *cis*-cyclohexyltrisiloxanolate the cyclohexyl groups occupy all the space available and are distributed with their rings facing one another.

Table 4.2 reports the significant bond angles in the phenylcyclotetrasiloxanolate obtained by Shchegolikhina and the cyclohexylcyclotrisiloxanolate obtained in our laboratory:

Phenylcyclotetrasiloxanolate		Cyclohexylcyclotrisiloxanolate
Si3—O3—Si4 139.5	1	Si2—O2—Si1 137.47
Si2—O2—Si3 143.9		Si3—O4—Si2 131.54
Si1—O1—Si2 139.9		Si1—O6—Si3 135.03
Si1—O4—Si4 144.4	2	Si5—O8—Si4 131.71
		Si6—O10—Si5 131.45
		Si4—O12—Si6 134.44

Table 4.2 – Selected bond angles (°) in phenylcyclotetrasiloxanolate and cyclohexylcyclotrisiloxanolate.

In the cyclohexylcyclotrisiloxanolate column are listed the data from the two distinct rings present in the cell. It is not surprising that the angles in the T_3 and T_4 ring structures are different. What is surprising is that there are large differences between the structures of two adjacent triols. The internal angles in the phenylcyclotetrasiloxanolate, even if they are not exactly the same, have a certain uniformity within the structure itself, maintaining a certain degree of symmetry. In fact, the angles for the two oxygen atoms marked with an odd number are essentially the same as are the angles for the oxygen atoms marked with an even number. In the cyclohexylcyclotrisiloxanolate this symmetry is not reflected in the structure of the

triol. In fact, in such structures, the angles are not even the same between the two triols.

This difference in angles within the ring could be another reason why the three membered siloxane ring is not as stable as the four membered siloxane ring. In fact, when Shchegolikhina reacted the phenylcyclotetrasiloxanolate with TMS-Cl the corresponding TMS-derivatised cyclotetrasiloxane was obtained, after crystallisation. However, when cyclohexylcyclotrisiloxanolate was reacted with TMS-Cl, crystallisation gave the corresponding TMS cyclo*tetra*siloxane instead of the TMS cyclo*tri*siloxane, (as discussed in Section 4.6.1) confirming the low stability of the cyclohexylcyclotrisiloxane ring.

4.4.8– Synthesis of cyclopentyltrisiloxanolate.

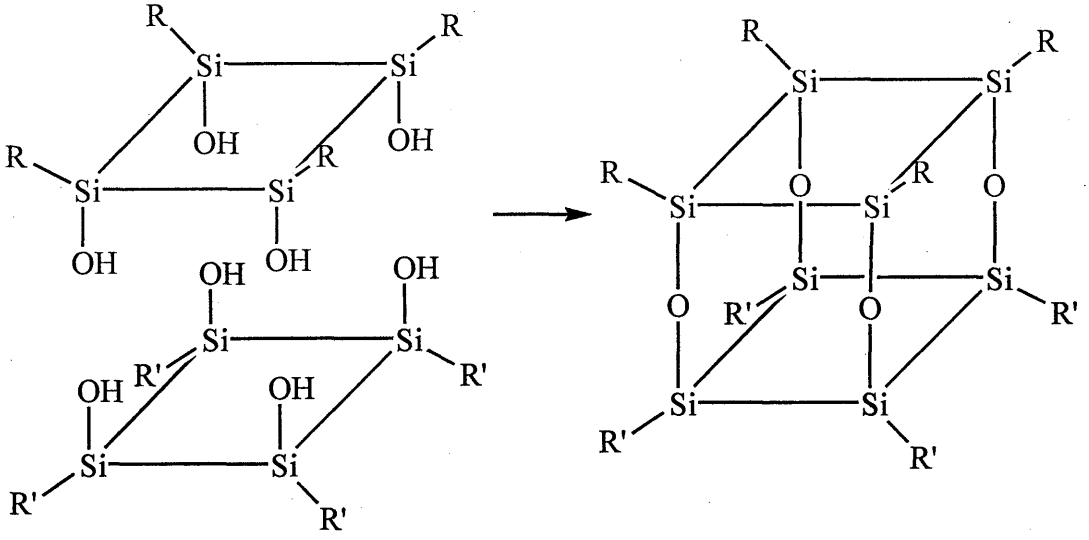
Shchegolikhina's procedure was repeated using cyclopentyltrichlorosilane as the starting material. This time the ^{29}Si-NMR gave a resonance with a chemical shift of –58.18 ppm, close enough to the corresponding cyclohexyltrisiloxanolate to suggest a similar product was formed. As with the cyclohexyltrisiloxanolate, we attempted to obtain the X-Ray crystal structure but, we could not obtain sufficiently good crystals to give a clear X-Ray diffraction pattern.

4.5 – Reactions of alkyl- and arylcyclotetrasiloxanetetraols.

As previously discussed, a cyclic *cis*-tetraol represents a molecule with a great potential for developing cage structures. For example, the tetraol is a good starting

material to synthesise T_8, since condensation of two molecules of *cis*-phenyltetraol should give phenyl-T_8.

Another exciting possibility is to synthesise T_8 molecules with different functionalities. For example, this method could be employed to synthesise a variety of *cis*-tetraols and condensation of two different tetraols will lead to a mixture of T_8 compounds.



Scheme 4.12 - Scheme of condensation of two different tetraols.

However, reaction between two different tetraols is likely to lead to a mixture of two homoT_8 cages and one heteroT_8 cage which may be difficult to separate. We thus decided to use a different strategy to prepare heteroT_8 cages and employ the tetraol as a scaffold and build the cages by addition of individual silicon units.

Shchegolikhina has reported the reaction of *cis*-phenyltetraol with TMS-Cl. The oxygen atoms of the tetraol attack the silicon atom of the TMS-Cl via a nucleophilic substitution, such that the OH group in the tetraol is converted into an O-TMS group. We thus reacted the *cis*-phenyltetraol with a range of dichloro- and trichlorosilanes.

4.5.1 – *cis*-Phenyltetraol + $RSiCl_3$.

One of the first reactions performed between the *cis*-phenyltetraol and trichlorosilanes involved cyclohexyltrichlorosilane. The reason for this was because cyclohexyl-T_6 and T_8 cages are well characterised structures, as are with phenyl T_6 and T_8 analogues; thus, any heterocage structures or potential cage compounds containing these units should be easy to identify.

An amount of trichlorosilane equivalent to the proportion of silicon in the tetrol was added, dropwise under an inert atmosphere of nitrogen, to a solution of the *cis*-phenyltetrol in THF together with proton sponge, which was added to neutralise the HCl formed during the reaction. As the tetrol did not dissolve in the THF immediately the mixture was stirred for some time until the white powder was completely dissolved. A white solid precipitated after a few minutes due to the protonation of the proton sponge.

A fraction of this solution was withdrawn and the solvent removed by flushing nitrogen through the solution and the resulting crude mixture was analysed by ^{29}Si-NMR. Despite the poor quality of the spectrum (due to the presence of the protonated proton sponge) and the presence of a small amount of resin, two resonances could clearly be seen with chemical shifts of –55.5 ppm and –75.7 ppm respectively, in a ratio of about 1:2. This was unexpected because, if the product was that predicted in Scheme 4.12 we would expect two peaks with different chemical shifts but in the same ratio due to the presence of the same number of silicon atoms in the two different environments. The chemical shifts suggested that the product obtained was a chloro compound, and thus the product was hydrolysed, in order to convert the

chlorine into an OH and therefore make it easier to handle. An amount of water equivalent to the silicon in the tetraol and in the trichlorosilane was dissolved in acetone and added to the crude mixture previously obtained. After two hours stirring, a fraction of the solution was analysed by ^{29}Si-NMR and, again, the spectrum, showed two resonances but this time more clearly with a chemical shift of –49.7 ppm and –68.4 ppm respectively, though the ratio was again 1:2. The chemical shift of – 68.4 ppm suggests that the structure is likely to be of a T_6 type because it is so close to the chemical shift of phenyl-T_6, –66.9 ppm. The corresponding shift in the phenyl T_8 cage is –79.7 ppm. The integration ratio and the chemical shifts suggest a cage with four silicon atoms carrying the phenyl sustituent and two silicon atoms with the cyclohexyl group. The silicon atom attached to the sp^2 carbon has the lower chemical shift (-68.4 ppm) and is double in size compared to the peak with a chemical shift of –49.7 ppm.

The solid, consisting of protonated proton sponge, was separated from the mixture by filtration, the solvent evaporated by rotary evaporation and the oily product analysed by MALDI-TOF. Theoretical calculations based on a T_6 cage carrying four phenyl groups and two cyclohexyl groups on the silicon atoms, gave a molecular mass of 786. The MALDI-TOF analysis showed a peak at m/z 971 which is close to the sum 804+168 where 168 is the molecular mass of the DBH (2,5-dihydroxybenzoic acid) used as the matrix in this analysis.

The m/z value of 804 is not far from that expected. In fact, it matches the molecular mass of the supposed T_6 cage plus 18 (molecular mass of water). Adding a molecule of water to a T_6 cage would produce two OH groups in the molecule. The FT-IR analysis, showed a large band in the region of 3100 cm^{-1} confirming the presence of OH groups. Another piece of evidence comes from the ^{29}Si-NMR itself: the resonance with a chemical shift of –49.7 ppm was far higher than that expected for a cyclohexyl

T_6 cage, -56.6 ppm. Previous structures have shown that conversion of a Si—O—Si to Si—OH results in a shift of about 7–10 ppm. Indeed the cyclohexyltetrol gave a peak at –59.38 ppm.

In conclusion, we suggesty that the molecule obtained is likely to be one of the two structures shown in Figure 4.24:

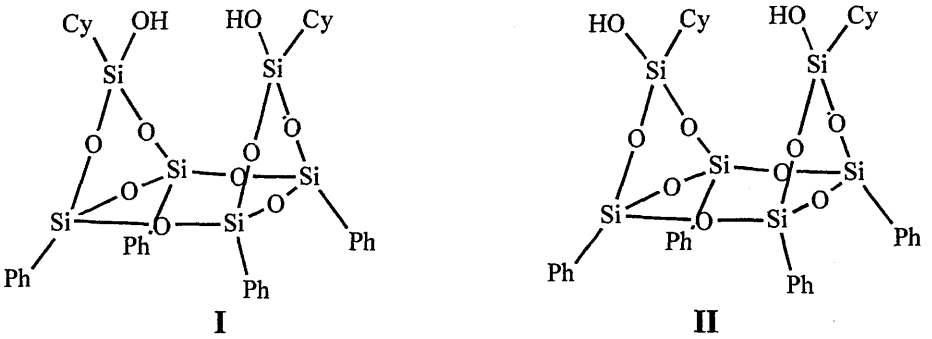


Figure 4.24

The analysis carried out on the product did not enable us to confirm unambiguously which of the two structures correspond to the product. We think that the most probable structure is the first structure because of the opportunity of forming intramolecular hydrogen bonds. Also compound **I** has two planes of symmetry giving just two peaks. However, in compound **II** the four SiPh atoms are not identical and similarly the two cyclohexyl-Si atoms are not identical giving two pairs of peaks in a ratio 1:1. Further analysis, as well as the calculation of the yield, were not possible because of the difficulty of isolating the product as a crystalline material.

The product obtained was reacted with DCC in anattempt to re-form the T_6 cage. However, analysis of the reaction mixture after treatment with DCC suggested that formation of T_6 cage had not occurred.

Reaction of an excess of cyclohexyltrichlorosilane with the *cis*-phenyltetraol gave a ^{29}Si-NMR spectrum with two signals in the same regions as that described above, but each signal comprised two resonances. The first set had chemical shifts at –49.8 ppm and -50.2 ppm and the second set had chemical shifts at -68.7 ppm and –69.5 ppm. The ratio between the first set of peaks and the second was again 1:2. Whilst in the previous experiment the most likely structure was compound **I**, this latter spectrum is consistent with compound **II** or a mixture of **I** and **II** if the chemical shifts in **II** overlap. This experiment suggests that if the reaction is performed in a 1:1 ratio (in equivalents) of *cis*-phenyltetraol/cychexyltrichlorosilane to TMSCl, structure **I** is preferred but, working with a large excess of the trichlorosilane structure **II** is preferred. It is not clear why this arises.

4.5.2 – *cis*-Phenyltetrasiloxanolate + R_2SiCl_2.

A range of dichlorosilanes were reacted with the tetrasiloxanolate but only when dimethyldichlorosilane was used did we get more interesting results. From the ^{29}Si-NMR of the crude mixture of the reaction it was possible to observe three major resonances plus a small amount of resin. The three resonances had chemical shifts of –3.5 ppm, -18.9 ppm and –67.9 ppm. From the spectrum it was not possible to quantify the ratio of the three resonances, but they were not of an equal size. The crude mixture was washed with hexane in order to separate the main product from the resin. Again the ^{29}Si-NMR exhibited the same resonances. The mixture was analysed by MALDI-TOF and the result was again quite interesting. The reaction product is a mixture of the phenyltetrol with its OH groups substituted by one, two, three or four Me_2SiCl- groups corresponding to the peaks at m/z 920 (tetra substitution), m/z 828

(probably a small peak not numbered) and m/z 736. The picture of the data obtained is shown in Figure 4.25. Owing to the presence of water in the atmosphere, the MALDI-TOF analysis, showed that some of the chlorines were hydrolysed to give the corresponding OH groups. Because of the complexity of the mixture it was not possible to separate the three products.

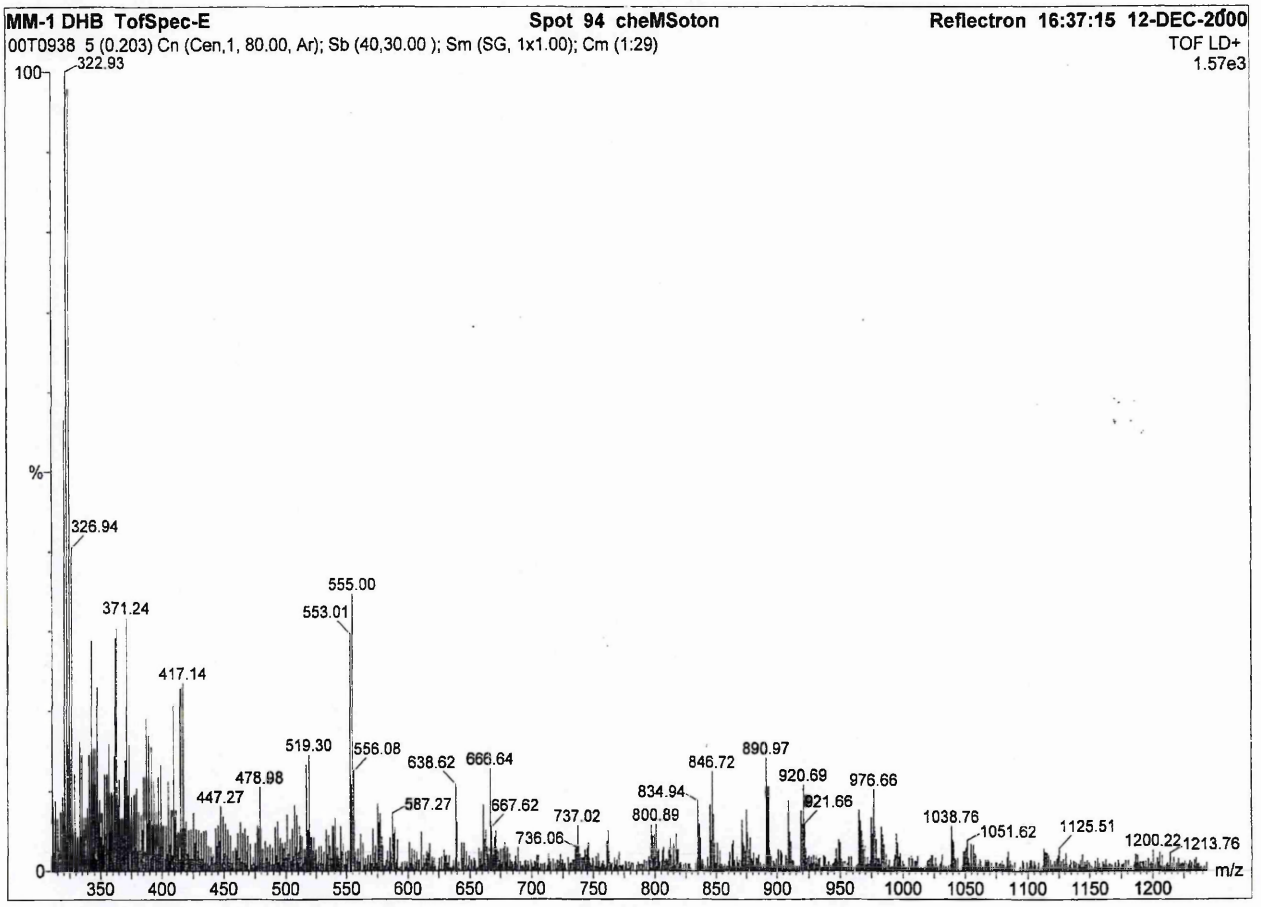


Figure 4.25

4.6 – Reactions of *cis*-cyclohexylcyclotetrasiloxanetriol/tetraol.

4.6.1 – *cis*-Cyclohexylcyclotetrasiloxanetriol/tetraol + R_3SiCl.

Several reactions involving the cis-cyclohexyltriol/tetraol were performed using chlorosilanes having a general formula of R_3SiCl. Following the Shchegolikhina procedure for characterising the cis-phenyltetraol, the cis-cyclohexyltetraol was reacted with TMS-Cl in the presence of pyridine and toluene. According to the ^{29}Si-NMR, the starting material was a mixture of the triol and the tetrol, giving resonances at –49.8 ppm and –58.4 ppm with a 1:1 ratio.

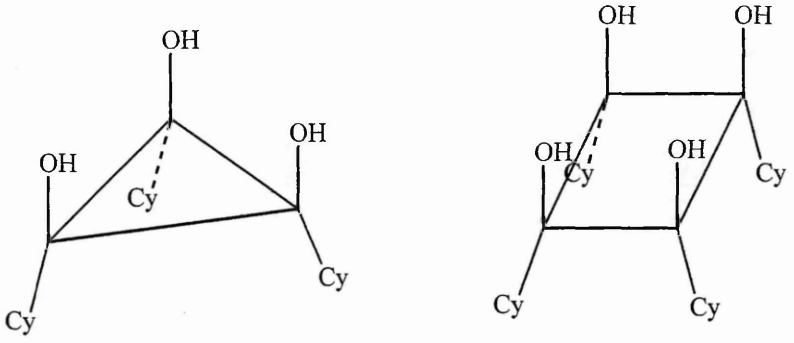


Figure 4.26

In solution the two silanols exist in some kind of equilibrium but only the triol formed crystals which were analysed by X-Ray crystallography. This is probably because of a difference in solubility between the two species in the recrystallising solvent.

The crystals obtained from the silylation reaction were purified by recrystallisation from a mixture of hexane/methanol and the X-Ray crystal structure of the product was obtained, as shown in Figure 4.27. This Figure shows the four siloxane groups in a ring where the cyclohexyl groups ensure the ring is almost planar. The cyclohexyl groups, again, lie on one side of the ring with the O-TMS groups on the other side.

Despite the possibility of rotation along the Si—C bond between the silicon of the ring and the carbon of the cyclohexyl group next to it, the carbon rings are equally symmetrically distributed. The same situation can be described for the four O-TMS group on the other side of the siloxane ring.

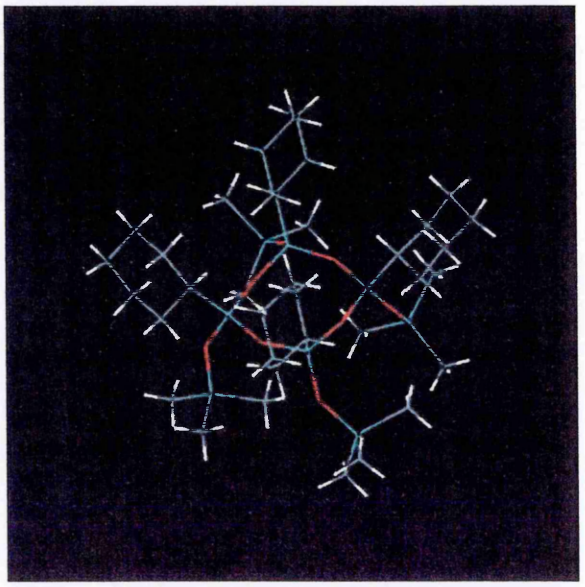
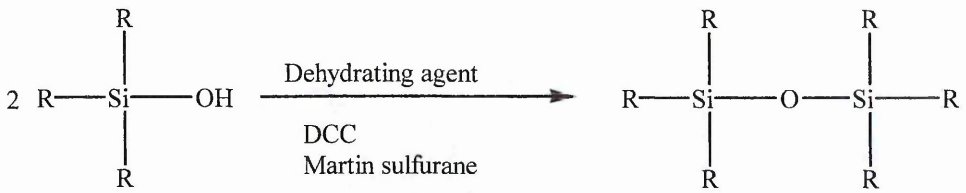


Figure 4.27 – Crystal structure of *cis*-cyclohexyltetratrimethylsiloxycyclotetra-siloxane

4.7 – Conclusion.

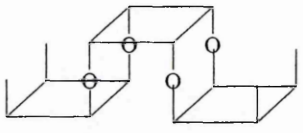
The condensation of two silanols can occur when a dehydrating agent is used. This reaction leads to a siloxane product with loss of one molecule of water for each pair of OH groups. A general condensation reaction of silanols is shown in the following Scheme 4.14:



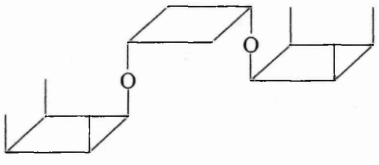
Scheme 4.14

Coupling two *cis*-tetrol rings or other type of fragments such as disiloxanes in order to form cages was not as straightforward as it seemed. The multifunctionality of the precursors leads to ladders and resins rather than ordered forms. Furthermore, several factors must be considered, such as concentration and possible interaction with the solvent as well as the dehydrating agent. When using DCC for example (but also other dehydrating agents), the dehydration does not necessarily occur within the two rings as expected. The possibility of matching all four OH groups in the two rings is actually quite unlikely to happen.

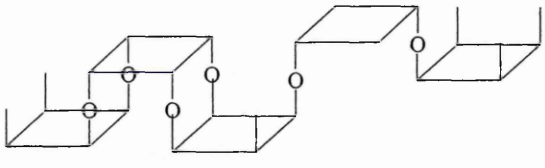
Figure 4.28 summarises some of the possible ways in which the *cis*-tetrasiloxanetetrols could condense:



Ladder-like combination



Linear combination

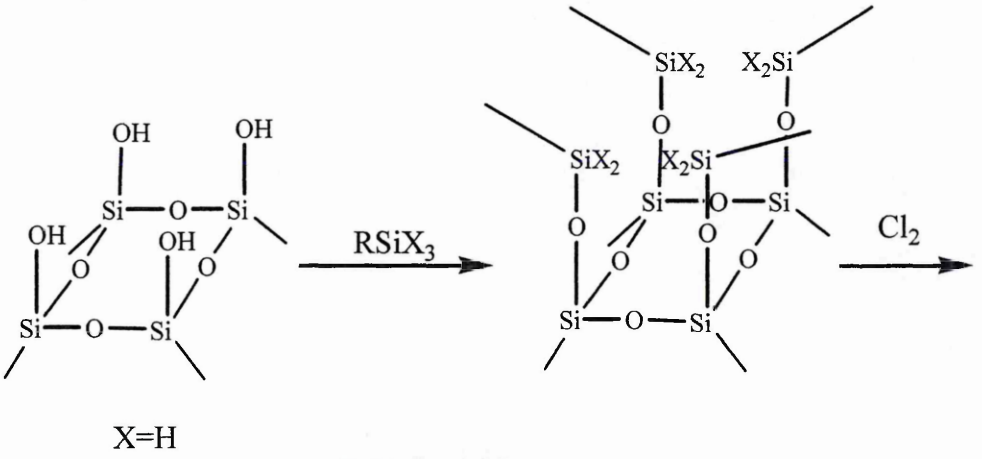


Mixed ladder and linear conbination

Figure 4.28 – Possible combination of tetrols after condensation.

It also clear that polyol rings and chains do not exist as discrete compounds in solution but give rise to a complex equilibrium mixture. For example, we have obtained an equilibrium mixture of T_4, T_6 and T_8 linear chains in solution and polyol T_3 and T_4 rings in solution. The stability of these species is often dependent upon the presence of water or alcohol to hydrogen bond with the silanols. Thus, the X-Ray crystal structure of the pure crystals shows the presence of a great deal of water and alcohol. This makes the use of dehydrating agents to couple such polyols very difficult since the dehydrating agent will preferably react with the water and/or alcohol. This subsequent dehydration could then alter the ring/chain equilibrium of the polyol such that the polyol species required to undergo the condensation may no longer be present.

A much better route seems to be the use of the tetrol or triols as a template scaffold to built cage precursors. For example, starting with phenyltetrol it would be possible to attach four silicon atoms with groups that could, subsequently, be converted into reactive groups and thus enable cage formation. An example of this new approach for cage synthesis is shown in Scheme 4.15:



X=H

Scheme 4.15

Work is in progress to develop this approach further.

CHAPTER 5

EXPERIMENTAL

5.1 – Instrumental analysis.

NMR

All NMR measurements were obtained using either a JEOL JNM LA 300 or JEOL EX400 FT spectrometer fitted with multinuclear probes. ^{13}C spectra were broad band decoupled. The pulse delay for ^{29}Si spectra was standardised at 15 s unless stated otherwise.

All spectra were recorded at room temperature, 20 °C, using deuteriochloroform ($CDCl_3$) dried over molecular sieves as solvent unless indicated otherwise. The internal NMR reference compound for 1H, ^{13}C, ^{29}Si spectra, (where used) was tetramethylsilane (TMS). In spectra where the reference compound was not used the reference was determined using the pre-determined data point for tetramethylsilane.

All chemical shift are reported in ppm from TMS.

Mass Spectrometry

Where possible the mass spectrum has been reported for all compounds. Analytical work within the group over a numbers of years has shown that it is often difficult to obtain mass spectra for particular organosilicon compounds such as cages or partial cages. This is often associated with the insolubility of such compounds.

Low resolution mass spectra were recorded on a VG20-250 mass spectrometer available at The Open University.

High resolution mass spectrometry was performed by the National Spectrometry Service Centre, based at the University of Wales, Swansea.

MALDI-TOF Mass Spectrometry

The Matrix Assisted Laser Desorption/Ionisation – Time of Flight (MALDI-TOF) analyses were performed by the mass spectrometry service at University of Southampton on a Tofspec2E instrument. Unless stated otherwise the analyses used DBH as the matrix and dichloromethane as the solvent.

Elemental Analysis

Microanalyses were performed by MEDAC limited. Microanalyses have been reported where possible. However work on organosilicon compounds over many years within the group has shown that it is often very difficult to obtain accurate elemental analysis for particular types of organosilicon compounds such as cages. Despite repeated submission of samples that have passed every other test of purity, it is often impossible to obtain satisfactory elemental analysis. This is thought to be a result of silicon carbide formation leading to carbon percentages that are lower than expected. Thus many elemental analyses have one elemental percentage that falls outside the accepted criteria and thus they have not been quoted.

Infra Red

FTIR spectra were carried out using either Perkin-Elmer 1710 or Nicolett 205 FT-IR spectrometers .

Unless otherwise indicated IR spectra were recorded using NaCl plates.

Melting Points

Melting points were determined on an Electrothermal Digital melting point apparatus and are uncorrected.

Gas Chromatography

The gas chromatograms were obtained using a Perkin Elmer Gas Chromatograph equipped with a methyl silicon bonded capillary column (25m, 5μ film thickness, 0.53 mm i.d.) and a flame ionisation detector. Chromatographic details are reported in subsequent sections.

GC/MS

The gas chromatograph used for the GC/MS analyses was a Finnigan VARIAN 3700 equipped with an ion trap detector. The column used in this gas chromatograph was a BP1 (non polar column – 15m, 0.5μ thickness, 0,32mm i.d.). Chromatographic details are reported in subsequent sections.

5.2 – Reagents and solvents.

The reagents used in this work were: DMSO, pyridine N-oxide, trioxysulfurpyridine complex, triphenylphosphine oxide, iodosobenzene, dimethyldichlorosilane, diphenyldichlorosilane, biphenyl, adamantane, T_8, 1-octene and methyltrichlorosilane. All the reagents used are commercially available (Aldrich Chemical Company, Lancaster Ltd. and Gelest Ltd.), except iodosobenzene and T_8, and the purity of this commercial products was assessed by ^{13}C and ^{1}H-NMR. The purity of the commercial silanes was also assessed by ^{29}Si-NMR. No further purification was necessary for all the commercially available reagents.

5.2.1 - Purification of Chloroform.

For all the chlorosilane reactions, commercial chloroform was used without further purification. In the iodosobenzene synthesis, dried chloroform was used. 200 ml of commercial chloroform was washed with water to remove the EtOH, dried with $CaCl_2$ and then refluxed. It was then distilled.

5.2.2 – Purification of DMSO.

The purity of commercial DMSO was assessed by ^{1}H-NMR and ^{13}C-NMR which suggested it did not require further purification. When used as a reagent, it required further drying so molecular sieves were added to the bottle in order to reduce the amount of water.

^{1}H-NMR – δ 1.99 ppm (s, CH_3).

^{13}C-NMR – δ 40.81 ppm (s, CH_3)

5.3 - Synthesis of Iodosobenzene[204].

In a 250 ml three-necked round bottomed flask, equipped with a mechanical stirrer, an inlet tube and an outlet tube carrying a calcium chloride guard tube, was added a solution of dry chloroform (37.5 ml) and iodobenzene (25.5 g). The solution was stirred and cooled to –5 °C. Chlorine gas was passed through the solution until an excess was present. The yellow crystalline (iodobenzenedichloride) solid was filtered, washed with chloroform and dried in air (yield about 90%).

The intermediate iodobenzenedichloride (30 g.) was placed in a large mortar with anhydrous sodium carbonate (50 g.). Then crushed ice was added and the mixture ground until all the ice had melted and a thick paste obtained. The paste was transferred to a beaker and a 5 M solution of NaOH (70 ml) was added in 10 ml portions followed by vigorous stirring. Water (60 ml) was added to the paste and the mixture allowed to stand overnight. The mixture was filtered and the excess liquor removed. The solid was transferred to a beaker and stirred with water (150 ml) and filtered; this operation was repeated. Finally the product was washed with water (100 ml) and chloroform (20 ml) to remove any iodobenzene dichloride and dried in air and then under vacuum (yield approximately 50 %). The iodosobenzene obtained was characterised by ^{1}H and ^{13}C-NMR and by GC/MS. All chemical shifts were in agreement with those reported in the literature.

5.4 - Synthesis of H_8T_8 (Octahydrogenosilsesquioxane).

In a two necked round bottom flask was placed a mixture of hexane (700 ml) and toluene (100 ml). In the same flask was added a solution of anhydrous ferric chloride (100 g) in conc. hydrochloric acid (40 ml) and methanol (80 ml). This mixture was stirred using a magnetic stirrer. A solution of trichlorosilane (44 ml) in hexane (300 ml) was added using a pressure equalising dropping funnel over a period of 6.5 h. Then the mixture was stirred for an additional 30 min. After this period, the upper hexane layer was removed and the suspended yellow solid transferred to another flask. Sodium carbonate (28 g) was added and the solution stirred overnight. After filtration, the filtrate volume was reduced by rotary evaporation to about 100 ml and the resulting solution placed in a freezer to crystallise. The ^{29}Si-NMR resonance at -84

ppm confirmed that the white crystalline material obtained was T_8. Yield approximately 7.78 %.

^{1}H-NMR δ 4.26 ppm (s, H).

^{29}Si-NMR δ –84 ppm.

All spectral data were in agreement with published data.

5.5 – Synthesis of Octyl-T_8 via hydrosilylation.

T_8 (0.21 g, 0.5 mmol) and 1-octene(0.45 g, 4 mmol) were added to a vial equipped with a stopper. 10 % solution of H_2PtCl_6 in isopropylalcohol (10 μl) was added to the reaction mixture, which was stirred at a temperature of 80° C. The octyl-T_8 formation was followed by monitoring the disappearance of the Si—H peak in the IR.

The octyl-T_8 obtained was purified by column chromatography, using silica gel with hexane as eluent. The white crystals obtained were analysed by ^{29}Si-NMR. The resonance at -66 ppm confirmed the presence of octyl-T_8.

^{29}Si-NMR: –66.63.

^{1}H-NMR: 0.6 (t, CH_2), 0.9 (t, CH_2), 1.3 (s, CH_3).

^{13}C-NMR: 11.97 (s, CH_2), 14.15 (s, CH_2), 22.73 (s, CH_2), 22.80 (s, CH_2), 29.29 (s, CH_2), 29.35 (s, CH_2), 31.98 (s, CH_2), 32.72 (s, CH_3).

5.6 – Reactions of dichlorosilanes with oxygen donor compounds.

5.6.1 – Analysis of the product of reactions.

All the reactions were analysed by GC and/or GC/MS. The GC was set up with the following temperature program:

40 °C (0 min) then increased to 150 °C (5 min) at 10 °C/min and then increased to 200 °C (1 min) at 10 °C/min;

injector temperature 270 °C;

detector temperature 275 °C.

For the GC/MS the following conditions were used:

50 °C for 10 min increased to 250 °C for 5 min at 10 °C/min.

All the retention times were assigned by injection of a standard solution (where possible) and the structure was further confirmed by injection on the GC/MS.

The retention times for D_3, D_4 and D_5 (on the GC) were: 3.81 min, 6.90 min and 9.61 min respectively.

The mass spectra for D_3, D_4 and D_5 in all cases show the characteristic fragmentation M-CH_3, which represents the base peak.

10 µl of the reaction mixture, for each reaction, were injected onto the gas-chromatograph. The first injection was after 2-3 min of reaction in all cases. For all the reactions the injection was repeated every hour, except when iodosobenzene was used, in which case the injection was repeated every 10 min.

5.6.2 – DMSO + Me_2SiCl_2

Me_2SiCl_2(1.17 g, 9 mmol) and biphenyl (0.97 g, 6 mmol) were dissolved in $CHCl_3$ (25 ml) and the stirred solution was cooled to -30 °C. 9 mmol (0.72 g) of DMSO was added dropwise to the cooled solution under nitrogen, to avoid the increase in the temperature. The reaction mixture was stirred until it reached room temperature, and then stirred for a further 5 hours. The reaction mixture was analysed by GS/MS and the retention times of the products were in agreament with the expected retention time of D_3, D_4 and D_5.

5.6.3 – Ph_3PO + Me_2SiCl_2

Triphenylphosphine oxide (2.62 g, 9 mmol) was added to a solution of Me_2SiCl_2 (1.22 g, 9 mmol) and biphenyl (0.97 g, 6 mmol) in of $CHCl_3$(25 ml), under nitrogen, at room temperature. The reaction mixture was stirred for 5.5 hours and then analysed by GC/MS.

5.6.4 - Iodosobenzene + Me_2SiCl_2

To a solution of Me_2SiCl_2 (0.30 g, 2.25 mmol) and biphenyl (0.24 g, 6 mmol) dissolved in $CHCl_3$ (25 ml), under nitrogen, was added to iodosobenzene (0.50 g, 2.25 mmol) and the reaction mixture was stirred for 50 min at room temperature and then analysed by glc/ms.

5.6.5 – Sulfur trioxide Pyridine-complex + Me_2SiCl_2

Sulfur trioxide pyridine-complex (1.46 g, 9 mmol) was added to a solution of Me_2SiCl_2 (1.20 g, 9 mmol) and biphenyl (0.97 g, 6 mmol) in $CHCl_3$ (25 ml), under nitrogen, and stirred for 2 h at room temperature and then analysed by GC/MS.

5.6.6 – Pyridine N-oxide + Me_2SiCl_2

Pyridine N-oxide (0.87 g, 9 mmol) was added to a solution of Me_2SiCl_2 (1.17 g, 9 mmol) and biphenyl (0.97 g, 6 mmol) dissolved in $CHCl_3$ (25 ml), under nitrogen, at room temperature and stirred for 4 h and then analysed by glc/ms.

5.7 – Reaction of DMSO and dimethyldichlorosilane in different solvents.

Reaction in water. Me_2SiCl_2 (1.17 g, 9 mmol) were dissolved in water (25 ml) then DMSO (0.72 g, 9 mmol) was added dropwise to this solution. The two phase solution obtained was stirred over a period of three hours then the product was extracted using CH_2Cl_2. The solvent of the organic layer was evaporated by rotary evaporation and a fraction of the product was dissolved in chloroform and the solution obtained analysed by GC. No relevant peaks were observed.

Reaction in hexane. Me_2SiCl_2 (1.17 g, 9 mmol) were dissolved in hexane(25 ml). This solution was then cooled to 0 °C and then DMSO (0.72 g, 9 mmol) was added dropwise to this solution. A white solid formed, identified as frozen DMSO, which disappeared when the reaction mixture was warmed to room temperature. After

three hours the crude mixture was injected onto the GC. No improvement in the yield of D_3 was observed.

5.8 – Reaction of DMSO and Me_2SiCl_2 with a ratio of 1:1.5.

This reaction was performed using the same methodology as previously described for the ratio 1:1. Only the amount of the dimethydichlorosilane was increased. Again biphenyl was used as the internal standard. The crude reaction was analysed using the GC over a period of five hours by injecting the crude reaction mixture every 0.5 h.

5.9 – Reactions involving DMSO and disubstituted dichlorosilanes.

5.9.1 - DMSO + $MeHSiCl_2$

A solution of $MeHSiCl_2$ (1.03 g, 9 mmol) in of chloroform (12.5 ml) was cooled to a temperature of –30 °C and then a cooled solution of DMSO (0.72 g, 9 mmol) in chloroform (12.5 ml)was added. The mixture was stirred over a period of 3.5 h and subsequently analysed by GC and ^{29}Si-NMR.

5.9.2 - DMSO + $PhMeSiCl_2$

A solution of DMSO (0.72 g, 9 mmol) in $CHCl_3$ (12.5 ml) was cooled to –30 °C and added to a solution of (1.72 g, 9 mmol) of $PhMeSiCl_2$ in chloroform (12.5 ml) and

stirred overnight. After this time the crude mixture was analysed by GC and ^{29}Si-NMR.

5.10 – Halogenation of anisole.

Anisole (0.95 g, 9mmol) was added to a solution of $(CH_3)_2SiCl_2$) (1.17 g, 9 mmol) (or $(CH_3)_2SiBr_2$(1.95 g)) in chloroform (25 ml) and 9 mmol of each oxygen donor compound. The reaction mixture was stirred and refluxed under argon for 24 hours. The reaction was followed by GC. 25 µl of the solution was quenched in 250 µl of sodium bicarbonate and extracted with 2 ml of dichloromethane. The dichloromethane solution was injected onto the GC.

The instruments used for this analysis was a GC 600 VEGA series 2 (CARLO ERBA) equipped with a 25 m. column, 0.32 ID made by S.G.E.; the conditions were as follows: 55 °C (1 min), then increasing 10 °C/min up to 250 °C. The retention times were confirmed by injection of standard solutions of the expected reaction products, 2-chloroanisole and 4-chloroanisole (or the corresponding bromoanisoles).

5.11 – Reaction of trichlorosilanes with oxygen donor compounds.

All new compounds from this work are highlighted with a "*" on the title.

Octyltrichlorosilane + DMSO (1:1).

(2.25 g, 9 mmol) of octyltrichlorosilane were dissolved in chloroform (12.5 ml) and to this solution was added a solution of (0.72 g, 9 mmol) of DMSO. After three hours of reaction the ^{29}Si-NMR revealed no relevant resonances.

Octyltrichlorosilane + Pyridine N-oxide (1:1). Octyltrichlorosilane (2.25 g, 9 mmol) were dissolved in chloroform (12.5 ml) and to this solution was added a

solution of DMSO (0.72 g, 9 mmol). After three hours of reaction the ^{29}Si-NMR revealed no relevant resonances. After 24 h the ^{29}Si-NMR analysis did reveal a small resonance with a chemical shift of –54 ppm.

Octyltrichlorosilane + Iodosobenzene (1:1). Octyltrichlorosilane (2.25 g, 9 mmol) were dissolved in chloroform (12.5 ml) and to this solution was added a solution of iodosobenzene (1.98 g, 9 mmol). After 24 h of reaction the ^{29}Si-NMR revealed no relevant resonances. The GC analysis was also inconclusive.

Octyltrichlorosilane + Trioxysulfur Pyridine complex (1:1). Octyltrichlorosilane (2.25 g, 9 mmol) were dissolved in chloroform (12.5 ml) and to this solution was added a solution of trioxysulfur pyridine complex (1.46 g, 9 mmol). After three h of reaction the ^{29}Si-NMR revealed no relevant resonance.

Octyltrichlorosilane + Triphenylphosphine oxide (1:1). Octyltrichlorosilane (2.25 g, 9 mmol) were dissolved in chloroform (12.5 ml) and to this solution was added a solution of of DMSO (0.72 g, 9 mmol). After three h of reaction the ^{29}Si-NMR revealed no relevant resonances.

5.11.1 – Synthesis of R-T_6.

Synthesis of hexaoctylhexasilsesquioxane(3.6).*

A solution of 55.29 mmol (4.32 g) of DMSO in 25 ml of chloroform was added dropwise to a solution containing 27.01 mml (6.69 g) of octyltrichlorosilane dissolved in 50 ml of chloroform (total volume of solvent 75 ml), under an atmosphere of N_2, during which the temperature of the reaction mixture increased to 47 °C. The solution became cloudy during the addition and then clear. The mixture was stirred for a further 24 h. An oily looking compound was formed on the surface of the chloroform.

The reaction mixture was washed with plenty of water in order to remove the DMSO by-product then the organic layer was dried over magnesium sulfate, filtered and the solvent reduced in volume by rotary evaporation. The crude reaction mixture was purified using a 80 × 2.5 cm chromatography column packed with alumina and eluted with chloroform. The solvent from the fractions containing the product was evaporated by rotary evaporation. A gel like product was obtained. Yield approximately 24.5 %.

Elemental analysis OctylT$_6$: Calc. (found) for $C_{48}H_{102}Si_6O_9$: C, 58.18 (58.03); H, 10.30 (10.53).

NMR OctylT$_6$: ^{29}Si-NMR -54.18 (s); ^{1}H-NMR: 0.10 ppm (t, CH_2), 0.36 (t, CH_3; J 11), 0.74 (m, CH_2); ^{13}C NMR 11.36 (s, CH_2), 14.07 (s, CH_2), 22.28 (s, CH_2), 22.65 (s, CH_2), 29.23 (s, CH_2), 30.85 (s, CH_2), 31.91(s, CH_2), 32.54 (s, CH_3).

Mass Spectrometry OctylT$_6$: 1013 $[M+Na]^+$,

Synthesis of hexa-7-octenylhexasilsesquioxane (3.7). *

55.29 mmol (4.32 g) of DMSO were dissolved in 25 ml of chloroform and added to 23.73 mmol (5.83 g) of 7-octenyltrichlorosilane dissolved in 50 ml of $CHCl_3$ under an inert atmosphere of N_2. During the addition, the temperature of the solution increased to 45 °C. The solution obtained was stirred for 24 h. After this time, the reaction mixture was washed with water, to remove the DMSO by-products, and then eluted through a 2.5 × 80 cm chromatography column packed with silica gel treated with TMS-Cl (see Section 5.12) and using chloroform as eluent. The solvent from the fractions containing the product was evaporated by rotary evaporation.

The NMR analysis of the residue was not satisfactory.

Synthesis of hexa-3-cyanopropylsilsesquioxane (3.8). *

A solution containing 55.29 mmol (4.32 g) of DMSO and 25 ml of chloroform was added to a solution containing 27.09 mmol (5.49 g) of cyanopropyltrichlorosilane under an atmosphere of nitrogen. During the addition, an increase of the temperature to 45 °C, was observed. The mixture was stirred for 24 h and then analysed by NMR. Numerous attempts to obtain a pure product failed to give satisfactory results.

Crude mixture data: ^{29}Si-NMR δ -55.47 ppm (s); ^{1}H-NMR: δ 0.90 ppm (s, C**H**$_2$-Si), δ 1.81 ppm (s, C-C**H**$_2$-C), δ 2.40 ppm (s, C**H**$_2$-CN); ^{13}C NMR δ 14.87 ppm (s, CH_2), δ 51.81 ppm (s, CH_2), δ 77.20 ppm (s, CH_2), δ 118.89 ppm (s, CN).

Synthesis of hexa-[3-(4-methoxyphenyl)propyl]hexasilsesquioxane (3.9).*

To a solution of 26.97 mmol (7.65 g) of 3-(4-methoxyphenyl)propyltrichlorosilane dissolved in 50 ml of chloroform was added, dropwise and under an inert atmosphere of N_2, 55.29 mmol (4.32 g) of DMSO dissolved in 25 ml of chloroform. The temperature was observed to increase to 42 °C. The solution obtained was stirred for 24 h.

The solvent was evaporated using a rotary evaporator. The crude mixture was passed through a chromatography column packed with silica gel treated with 5%, (by weight of silica gel) of TMS-Cl (see Section 5.12). The silica gel was washed with excess chloroform before use and chloroform was also used as eluent.

The fractions containing the desired product, identified by spotting a TLC plate, were collected and the solvent evaporated. The product was finally recrystallised in a mixture of chloroform (added until complete dissolution of the solid) and sufficient

hexane to initiate the crystallisation. The crystalline product was sufficiently pure to enable a single crystal X-ray structure to be determined.

NMR 3-(4-methoxyphenyl)propylT$_6$: ^{29}Si-NMR δ -54.42 ppm (s); ^{1}H-NMR: δ 0.70 ppm (t, CH_2; J 11), δ 1.68 ppm (m, CH_2; J 11), δ 2.53 ppm (t, CH_2; J 11), δ 3.73 ppm (s, CH_3), δ 6.73 ppm (d, CH; J 6), δ 6.87 ppm (d, CH; J 7); ^{13}C NMR δ 11.05 ppm (s, CH_2), δ 24.46 ppm (s, CH_2), δ 37.69 ppm (s, CH_2), δ 55.37 ppm (s, CH_3), δ 113.79 ppm (s, CH), δ 129.44 ppm (s, CH) , δ 134.21 ppm (s, C), δ 157.83 ppm (s, C).

Synthesis of hexabenzylhexasilsesquioxane (3.10). *

A solution of 26.88 mmol (6.05 g) of benzyltrichlorosilane in 50 ml of $CHCl_3$ was added dropwise to a solution containing 55.29 mmol (4.32 g) of DMSO dissolved in 25 ml of $CHCl_3$ under an inert atmosphere of nitrogen. An increase in the temperature to 37 °C was observed during the addition. The mixture was stirred for a further 24 h. The solvent was evaporated and the crude mixture eluted in a column packed with silica gel (50 g) treated with 5 % TMS-Cl (see Section 5.12) using chloroform as the eluent. The fractions containing the product, identified by spotting a TLC plate, were collected and the solvent evaporated using a rotary evaporator.

NMR BenzylT$_6$: ^{29}Si-NMR δ -59.00 ppm (s); ^{1}H-NMR: broad peaks in the region of 2 ppm and in the region of 7.5 ppm (m, CH); ^{13}C NMR δ 32.89 ppm (s, CH_2), δ 126.54 ppm (s, C), δ 128.76 ppm (s, 2CH), δ 129.27 ppm (s, 2CH), δ 132.03 ppm (s, CH).

Synthesis of hexa-*t*-butylhexasilsesquioxane (3.11). *

A solution of 8.98 mmol (1.72 g) of *t*-butyltrichlorosilane in 12 ml of $CHCl_3$ was added dropwise to a solution containing 18.03 mmol (1.42 g) of DMSO dissolved in

13 ml of $CHCl_3$. No appreciable increasing of the temperature was observed during the addition. The mixture was stirred for a further 24 h.

The solvent was evaporated and the crude mixture eluted in a column packed with silica gel (50 g) treated with 5 % TMS-Cl (see Section 5.12) using chloroform as the eluent. The fractions containing the product, identified by spotting a TLC plate, were collected and the solvent evaporated using a rotary evaporator.

NMR *t*-butylT_6: ^{29}Si-NMR broad peak in the region of –56.78.

^{1}H-NMR and ^{13}C-NMR analysis display the tytpical pattern of resin.

Synthesis of Hexahydrogenohexasilsesquioxane (3.12). *

55.29 mmol (4.32 g) of DMSO dissolved in 25 ml of chloroform was added dropwise, under an inert atmosphere of nitrogen, to a solution of 26.64 mmol (3.57 g) of $HSiCl_3$ dissolved in 50 ml of chloroform to give a total volume of 75 ml. During the addition the temperature increased to 60 °C. After the first half hour, the formation of a gel in the mixture was observed. The solution was stirred for 24 h and, subsequently, the crude mixture analysed.

^{29}Si-NMR – no peaks observed.

^{1}H-NMR – δ 1.91 ppm (t), δ 2.04 ppm (s), δ 2.22 ppm (s), δ 2.45 ppm (s), 4.67 ppm (s), δ 7.19 ppm (s, CH solvent).

^{13}C-NMR – δ 15.11 ppm (s), δ 18.07 ppm (s), δ 51.88 ppm (s).

Synthesis of hexamethylhexasilsesquioxane (3.13). *

55.29 mmol (4.32 g) of DMSO dissolved in 25 ml of chloroform was added dropwise to a solution of 26.64 mmol (3.94 g) of CH_3SiCl_3 dissolved in 50 ml of chloroform,

under an inert atmosphere of nitrogen, to give a total volume of 75 ml. During the addition the temperature increased to 60 °C. The solution was stirred for 24 h and, subsequently, the crude mixture analysed.

^{29}Si-NMR – broad peak in the region of – 55 ppm.

Synthesis of hexavinylhexasilsesquioxane(3.14). *

55.29 mmol (4.32 g) of DMSO dissolved in 25 ml of chloroform was added dropwise, under an inert atmosphere of nitrogen, to a solution of 26.64 mmol (4.26 g) of $CH_2CHSiCl_3$ dissolved in 50 ml of chloroform to give a total volume of 75 ml. During the addition the temperature increased to 60 °C. The solution was stirred for 24 h and, subsequently, the crude mixture analysed by ^{29}Si-NMR.

^{29}Si-NMR: -68.69 ppm (s), broad peak in the region of –70 ppm, and broad peak in the region of –80 ppm.

Synthesis of hexaphenylhexasilsesquioxane (3.15). *

A solution of 9.23 mmol (1.96 g) of phenyltrichlorosilane in 12 ml of $CHCl_3$ was added dropwise to a solution containing 18.03 mmol (1.42 g) of DMSO dissolved in 13 ml of $CHCl_3$ under an inert atmosphere of nitrogen. An increase in the temperature to 42 °C was observed during the addition. The mixture was stirred for a further 24 h. The solvent was evaporated and the crude mixture eluted in a column packed with silica gel (50 g) treated with 5 % TMS-Cl (see Section 5.12) using chloroform as the eluent. The fractions containing the product, identified by spotting a TLC plate, were collected and the solvent evaporated using a rotary evaporator.

NMR PhenylT$_6$: ^{29}Si-NMR δ -66.89 ppm (s); ^{1}H-NMR: broad peaks in the region of δ 7.42 ppm and in the region of δ 7.60 ppm; ^{13}C NMR δ 127.92 ppm (m, C), δ 131.38 ppm (m, 2CH), δ 134.23 ppm (m, 3CH).

Hydrosilylation of methyl 3,3-dimethylpent-5-enoate (synthesis of the corresponding trichlorosilane) (3.17). *

In a vial equipped with a stopper and a magnetic stirrer were placed 9.01 mmol (1.28 g) of methyl 3,3-dimethylpent-5-enoate, 0.25 ml of catalyst solution (hexachloroplatinic acid dissolved in isopropanol 0.02 M) and 9.17 mmol (1.22 g) of trichlorosilane. The mixture was stirred until complete addition of the trichlorosilane to the alkene had been confirmed by the disappearance of the Si—H in the IR spectrum. As the amount of catalyst (and similarly the amount of by-products) was too small to interfere in the subsequent reactions, no further purification was needed at this stage.

Yield approximately 85 %.

IR: The reaction was monitored until complete disappearance of the peak at 2250 cm^{-1} (Si-H).

Synthesis of hexa[3,3-dimethyl-4-(methoxycarbonyl)butyl]silsesquioxane (3.16). *

26.29 mmol (7.23 g) of methyl 3,3-dimethyl-5-trichlorosilylpentanoate were dissolved in 50 ml of choloroform and to this solution were added 55.29 mmol (4.32 g) of DMSO dissolved in 25 ml of $CHCl_3$ under an inert atmosphere of N_2. The

temperature increased to 45 °C during the addition and the solution was stirred for a further 24 h.

29Si-NMR: -56.62 ppm (s).

Synthesis of hexacyclopentylhexasilsesquioxane (3.18). *

A solution of 24.56 mmol (5.50 g) of cyclopentyltrichlorosilane in chloroform (25 ml), was slowly added under an atmosphere of nitrogen to a solution of 54.65 mmol (4.27 g) of DMSO dissolved in 50 ml of $CHCl_3$ so that the total volume was 75 ml. During the addition, the temperature increased to 47 °C. The mixture was stirred overnight, the solvent removed using a rotary evaporator and then analysed by ^{29}Si-NMR.

6.08 g of crude product mixture were placed in a column (18 × 3 cm) packed with alumina and eluted using chloroform. 0.35 g of pure product were collected after recrystallisation from hexane (9.4 %).

Elemental Analysis $CpPT_6$: Calc. (found) for $C_{30}H_{54}Si_6O_9$: C, 49.54 (49.55); H 7.48 (6.94).

NMR $CpPT_6$: ^{29}Si-NMR δ –54.37 ppm (s); ^{1}H NMR δ 0.96 ppm (m, CH) δ 1.45 ppm (m, $2CH_2$) δ 1.68 ppm (m, $2CH_2$); ^{13}C NMR δ 21.68 ppm (s, CH), δ 26.80 ppm (s, $2CH_2$), δ 26.97 ppm (s, $2CH_2$).

Mass Spectrometry $CpPT_6$ (EI): 726 $[M]^+$.

Synthesis of hexacyclohexylhexasilsesquioxane (3.19). *

27.02 mmol (5.88 g) of cyclohexyltrichlorosilane were dissolved in 25 ml of chloroform and this solution was added, dropwise and under an inert atmosphere of

nitrogen, to a solution containing 54. 91 mmol (4.29 g) of DMSO dissolved in 50 ml of chloroform to give a total volume of 75 ml. During the addition the temperature increased to 45 °C. The solution obtained was stirred for a further 24 h and subsequently analysed by ^{29}Si-NMR. The solvent was removed using a rotary evaporator.

4.85 g of the crude mixture were placed in a 20 × 2.5 cm column packed with alumina and eluted with $CHCl_3$. The desired product was collected in fractions 3 and 4. The solvent was evaporated from these fractions and the product recrystallised from hexane. The recrystallisation gave a total mass of pure product of 0.38 g. The final yield was 10.4%.

Elemental Analysis CyT_6: Calc. (found) for $C_{36}H_{66}Si_6O_9$: C, 53.3 (52.47); H, 8.15 (8.24).

NMR CyT_6; ^{29}Si- NMR δ -56.60; ^{1}H NMR δ 0.84 (m, CH), δ 1.22 (m, $2CH_2$), δ 1.57 (m, $2CH_2$), δ 1.70 (m, CH_2); ^{13}C-NMR: δ 22.6 (s, CH), δ 26.1 (s, $2CH_2$), δ 26.6 (s, $2CH_2$), δ 27.2 (s, CH_2)

Mass Spectrometry (Accurate Mass) CyT_6: 811 $[MH]^+$.

Synthesis of hexa*iso*butylhexasilsesquioxane (3.20). *

29.32 mmol (5.16 g) of *iso*butyl trichlorosilane dissolved in 25 ml of chloroform were added to 53.12 mmol (4.16 g) of DMSO dissolved in 50 ml of chloroform. The solution was stirred, under nitrogen, for 24 h. After this time the solvent was evaporated using a rotary evaporator and the crude mixture analysed by the usual techniques.

Elemental Analysis Iso-butT_6: Calc. (found) for $C_{24}H_{54}Si_6O_9$: C, 44.00 (44.41); 8.31 (8.69).

NMR Iso-butT_6: ^{29}Si-NMR: -55.42 ppm (s); ^{1}H NMR: δ 0.67 (d, CH_2) δ 0.96 (d, $2CH_3$), δ 1.78 ppm (m, CH); ^{13}C NMR: δ 22.00 ppm, δ 23.01 ppm, 25 ppm.

Mass Spectrometry (EI) Iso-butT_6: 654 $[M]^+$.

5.12 – Preparation of silica gel for column chromatography.

50 g of chromatography silica gel (Aldrich) were suspended in 200 ml of chloroform. To this suspension, 2.5 g (corresponding to 5% of the mass of silica gel) of TMS-Cl was added and the mixture was stirred over a period of half hour. The suspension obtained was used to pack a chromatography column of length 50 cm and 2.5 cm diameter. The chloroform was eluted and the silica gel was further washed with chloroform to remove the HCl formed. The column obtained using this procedure was then used to purify the T_6 compound with the appropriate eluent.

5.13 – Synthesis of *tert*-butyldisiloxanetetraol (Dow Corning procedure)

2.7 ml of MIBK and 3.6 ml of water were placed in a 3 necked round bottomed flask equipped with a thermometer and cooled to 15° C using an ice bath. A solution of 13 g *tert*-butyltrichlorosilane dissolved in 0.9 ml of MIBK were added to the mixture of solvents through a pressure equalising dropping funnel over a period of 20 min, ensuring that the temperature do not increase over 20° C. A white precipitate was

formed almost immediately and the mixture was stirred over night in order to increase the yield.

The precipitate was separated from the solution and dried in open air.

^{29}Si-NMR: -49.65 ppm (s); ^{1}H NMR: δ 0.96 (s, 18H CH_3), δ 4.83 ppm (s, 4H OH); ^{13}C NMR: δ 26.77 ppm (s, C), δ 49.04 ppm (m, $3CH_3$).

5.13.1 - Synthesis of cyclohexyldisiloxanetetraol (Dow Corning procedure).

The same procedure as described in the previous paragraph was followed using 2.6 g of cyclohexyltrichlorosilane dissolved in 0.9 ml of MIBK.

The precipitate formed was dried in open air and analysed by ^{29}Si-NMR giving a resonance of –51.26 ppm in agreement with an authentic sample provided by Dow Corning..

5.14 – Synthesis of *t*-butyldisiloxanetetraol (Unno's procedure).[186]

99.23 mmol (26 g) of *t*-butyldiphenylchlorosilane were added to a mixture of 35 ml of distilled THF and 46 ml benzene. A solution of 3.7 ml of NaOH in 50 ml of water was added to the mixture and the resulting mixture stirred for a period of 2 hours. The crude mixture was analysed by NMR and IR. The mixture was stirred overnight and after this time the organic layer was separated from the water and dried using $MgSO_4$. The solvent was then removed using a rotary evaporator. A colourless solution was obtained. The solvent was further reduced in volume and the solution left was left to crystallise.

NMR of the product obtained was not satisfactory.

5.14.1 – Condensation of cyclohexyldisiloxanetetraol (Unno's procedure with DCC).

1 mmol (0.576 g) of cyclohexyldisiloxanetetraol were dissolved in 5 ml of DMSO together with 3 mmol (0.62 g) of DCC in a round bottomed flusk and the mixture was stirred over a period of two days.

After this time a ^{29}Si-NMR was recorded but no relevant peak was observed except a forest of peaks in the region of –51 ppm confirming the presence of resin.

5.14.2 – Condensation of cyclohexyldisiloxanetetraol (Unno's procedure with Martin's Sulfurane).

1 mmol (0.25 g) of cyclohexyldisiloxanetetraol were dissolved in 50 ml of dried THF together with 8 mmol (4.25 g) of Martins Sulfurane in a round bottomed flusk and the mixture was stirred over a period of two days.

After this time a ^{29}Si-NMR was recorded. ^{29}Si-NMR: -68.5 ppm.

5.15 - Synthesis of cis-cyclotetrasiloxanetetraol.

Several methods have been reported for the synthesis of the *cis*-cyclotetrasiloxanetetrol. However, not all of them were successful in our hands.

Synthesis of tetraphenyl-cyclotetrasiloxane-*cis*-tetraol (Brown's procedure).[184]

A total of 1550 g of a mixture of water and ice were placed into a beaker equipped with an overhead stirring apparatus. 195.02 mmol (41.15 g) of phenyltrichlorosilane were dissolved in 70 ml of cold acetone and added to the mixture of water-ice with vigorous stirring and the resulting solution stirred for half an hour. The beaker was then placed in a fridge at a temperature of 1-2° C for a period of 2 d.

The cloudy solution was separated from the solid precipitate and then analysed as described in the text (Section 4.4.3 on page 146).

5.16 - Synthesis of cyclohexyldisiloxanetetraol (Unno's procedure via Grignard reagents).

In a three-necked round bottom flask equipped with a dropping funnel and a condenser, were placed (2.68) g of magnesium turnings, a magnetic stirrer and 15 ml of dried THF under an inert atmosphere of nitrogen. To this mixture was added, dropwise through a dropping funnel, a solution of 18.2 g of 4-methoxybromobenzene dissolved in 10 ml of dried THF. The temperature of the mixture was raised to reflux and the colour of the mixture turned brown.

15 ml of dried THF was added to the reaction mixture containing the p-methoxyphenylmagnesium bromide. To this solution was added 11.9 g of cyclohexyltrichlorosilane and the mixture was stirred overnight. While the trichlorosilane was added, the temperature of the mixture increased to achieve reflux. The solution obtained was filtered to remove the remaining Mg turnings and the

volume was reduced using a rotary evaporator. At the end of the reaction a white solid was observed with the Mg turnings and more solid was formed when the solvent was removed. Thus, 70 ml of toluene were passed through the filter such that the white solid, that was mixed with the Mg turnings, dissolved. To the final solution obtained was added 3.5 g of NaOH dissolved in 50 ml (solution of NaOH 1.75 M) of water and the resulting mixture stirred over a period of 1.5 h. The emulsion formed was broken by filtering the two layer system through a sinter glass funnel. The organic layer was separated from the water and dried using a rotary evaporator. The product obtained was analysed by ^{29}Si-NMR which gave a resonance at –24.84 ppm.

The solid was completely dried and subsequently dissolved in chloroform. Chlorine was then bubbled through the solution and again the crude mixture was analysed by ^{1}H, ^{13}C and ^{29}Si-NMR, however, the spectrum suggested a complex mixture had been formed.

Synthesis of tetraphenyl-cyclotetrasiloxane-*cis*-tetraol (Feher's procedure)[182]

500 g of water and 500 g of ice were placed in a beaker. 118.48 mmol (25 g) of phenyltrichlorosilane was dissolved in 45 ml of cold acetone and added to the mixture with vigorous stirring. The solution was stirred at 0° C for 4.5 h and then transferred to a fridge at a temperature of 5° C and left for 36 h.

The solid formed was separated from the solution and dried on the open bench. In order to dry the solid further it was placed in the oven at a temperature of 70° C.

5.17 - Synthesis of *cis*-phenyltetraol (Shchegolikhina's procedure).

In 150 ml of *n*-butanol were dissolved 39.3 g of phenyltriethoxysilane. To this solution was added 3 ml of H_2O and 6.5 g of NaOH. The mixture was stirred until all the sodium hydroxide was completely dissolved (it took about 1.5 h) under gentle heating. The temperature was then increased to reflux temperature and the solution was stirred for a further half hour. The solution was left to reach room temperature whereupon crystals started to form. The solution was placed in a fridge at 2 °C overnight in order to crystallise the product completely.

The crystals were rapidly filtered and 9.5 g of the resulting product were dissolved in 60 ml of toluene with an amount of ethanol sufficient to dissolve the solid completely (the volume of ethanol was up to 30 ml for this amount of solid). This solution was added to a solution of 500 ml of water and 9 ml of hydrochloric acid whereupon a white powdery looking solid was rapidly formed in the interphase between the organic and inorganic layer.

When the addition was completed, the solid was filtered and washed with a large amount of water in order to remove all the HCl. The amount of water used depended on the pH of the washing water. The yield was approximately 65 %.

The powder obtained was dried in the open air and stored in plastic bottles.

^{29}Si-NMR δ –59 ppm (s)

5.18 – Synthesis of sodium *cis*-cyclohexylcyclotetrasilanolate via cyclohexyl resin. *

25 ml of cyclohexyltrichlorosilane were dissolved in 25 ml of diethyl ether. The solution was added slowly to a mixture of 60 ml of diethyl ether, 10 g of ice and 15 ml of water all placed in a round-bottomed flask that was placed in an ice bath during the addition.

After the addition the mixture was stirred at room temperature for two hours and after this time the two phase solution was separated using a separatory funnel. In the interphase between the organic and the inorganic layer a crystalline solid was formed. It was filtered and analysed separately. The solvent of the organic layer was evaporated by rotary evaporation and a white resin looking solid was obtained.

0.022 mols (3 g) of this resin were dissolved in 20 ml of *n*-butanol and 0.022 mols (0.9 g) of NaOH were added to the solution solution together with 0.022 mols (0.4 g) of water; the mixture was stirred with a gentle heating until the sodium hydroxide was completely dissolved (it took more than one hour) then the solution was refluxed for a further half hour. After this time the solution was left to reach room temperature when the product began to crystallise. The flask was then placed in a fridge to crystallise more of the solid.

5.19 – Synthesis of cyclohexyltetrasiloxanetetrol. *

0.07 mols (11.6 g) of the sodium salt of cyclohexylcyclotetrasiloxanetetrol were suspended in 60 ml of toluene and, to this solution, a volume of ethanol was added, sufficient to dissolve the solid (about 25 ml). To this solution were added 27.7 mols

(500 ml) of water and 0.11 mols (9 ml) of hydrochloric acid. A white precipitate was formed almost immediately. It was then filtered and washed with plenty of water in order to remove the excess acid and subsequently with toluene in order to remove the water. The solid was then analysed.

^{29}Si-NMR –59.38 ppm.

5.20 – Synthesis of sodium *cis*-cyclopentylcyclotetrasilanolate via cyclopentyl resin. *

In 25 ml of diethyl ether were dissolved 25 ml of cyclopentyltrichlorosilane and this solution was added slowly to a mixture of 60 ml of diethyl ether, 10 g of ice and 15 ml of water all placed in a round-bottomed flask that was placed in an ice bath during the addition.

After the addition the mixture was stirred at room temperature for two hours and after this time the two phase solution was separated using a separatory funnel. In the interphase between the organic and the inorganic layer a crystalline solid was formed. This solid was filtered and analysed separately. The solvent of the organic layer was removed by rotary evaporation and 15.24 g of a white resin looking solid were obtained.

0.095 mols (3 g) of this resin were dissolved in 47 ml of *n*-butanol and 0.095 mols (3.8 g) of NaOH were added to the solution together with 0.095 mols (1.7 g) of water. The mixture was stirred with a gentle heating until the sodium hydroxide was completely dissolved (it took more than one hour) then the solution was refluxed for a further half hour. After this time the solution was left to reach room temperature when the product began to crystallise. The flask was then placed in a fridge to crystallise more of the solid.

5.21 – Reaction of sodium *cis*-phenylcyclotetrasilanolate with $RSiCl_3$.

Reaction of sodium *cis*-phenylcyclotetrasilanolate with $CySiCl_3$.

7.29 mmols (1 g) of the sodium salt of phenyltetrol was suspended in 100 ml of toluene. To this solution 2.96 mmols (0.6 g) of cyclohexyltrichlorosilane were added. The suspension became clear after a few seconds and it was left to stir for a further few minutes. The crude mixture was treated with water and proton sponge was added. The protonated proton sponge was filtered and, after the hydrolysis, the solvent of the crude mixture was evaporated. The mixture was analysed by NMR, IR and MALDI-TOF.

^{29}Si-NMR: δ –49.72 ppm, δ –68.49 ppm (ratio 1:2)

^{1}H-NMR: δ 1.21 (broad), δ 1.80 ppm (m, CH_2), δ 2.12 (s CH_2), δ 7.33 (broad m, Ph), δ (7.71 broad m, Ph).

^{13}C-NMR: δ 25.66 ppm (m, CH_2), δ 26.68 ppm (m, CH_2), δ 27.45 (m, CH_2), δ 127.77 ppm (m, Ph), δ 139.04 ppm (m, Ph), δ (134.24 (m, Ph).

IR (relevant peak): 3300 cm^{-1} (broad, OH)

MALDI-TOF: 912.77 (in DHB+Ag)

5.22 – Reaction of sodium *cis*-phenylcyclotetrasilanolate with R_2SiCl_2.

The reaction of sodium *cis*-phenylcyclotetrasilanolate with Me_2SiCl_2.

7.29 mmols (1 g) of the sodium salt of phenyltetraol was suspended in 100 ml of toluene. To this solution were added 3.28 mmols (0.4 g) of dimethyldichlorosilane. The suspension became clear after a few seconds and it was then left to stir for a further few minutes. The solvent of the crude mixture was then evaporated and the remaining solid analysed by NMR.

^{29}Si-NMR: broad peaks in the region of – 3.5 ppm, –18.9 ppm and –67.9ppm.

5.23 – Synthesis of the trimethylsilyl derivative of *cis*-cyclohexylcyclotetrasiloxane. *

0.06 mols (1.07 g) of the cyclohexyltetrasiloxanetetraol sodium salt were suspended in toluene. 0.022 mols (2.32 g) of trimethylchlorosilane and 0.016 mols (1.30 g) of pyridine were added to this mixture, which was then refluxed for half an hour. After this time the mixture was left to reach room temperature. The solid product (PyH^+ Cl^-) was filtered and the solution was washed with water until neutral pH. The organic layer was dried over $MgSO_4$ which was then filtered and the organic solvent removed by rotary evaporation. The yield was approximately 86%.

The solid product was analysed by X-ray crystallography. The results are reported in the appendix.

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APPENDIX

CRYSTAL STRUCTURES

A.1 - Crystal data and structure refinement of 3-(4-Methoxyphenyl) propyl-T_6

Table 1.

Identification code	00SRC614
Empirical formula	$C_{60}H_{78}O_{15}Si_{16}$
Formula weight	1207.76
Temperature	150(2) K
Wavelength	0.71073 ⊕
Crystal system	Monoclinic
Space group C2/c	
Unit cell dimensions	a= 45.9894(10) ⊕
	b= 8.0389(2) ⊕ β = 93.7700(13)°
	c= 16.5045(5) ⊕
Volume	6088.6(3) $⊕^3$
Z	4
Density (calculated)	1.318 Mg/m^3
Absorption coefficient	0.203 mm^{-1}
F(000)	2568
Crystal	Colourless plate
Crystal size	0.30 x 0.18 x 0.02 mm^3
Θ range for data collection	2.95 – 25.02°
Index ranges	-51≤h ≤51 , -9 ≤k ≤9 , -19≤l ≤19
Reflections collected	13068
Independent reflections	3254 [R_{int} = 0.0624]
Completeness to Θ = 25.02°	60.4%
Max. and min. transmission	0.9960 and 0.9417
Refinement method	Full-matrix least-squares on F^2
Data/ restraints / parameters	3254/ 12 / 367
Goodness-of-fit on F^2	1.073
Final R indices [$F^2>2\sigma(F^2)$]	R1 = 0.0536 , wR2 = 0.1403
R indices (all data)	R1 = 0.0792 , wR2 = 0.1569
Largest diff. Peak and hole	0.691 and –0.393 e $⊕^{-3}$

Diffractometer: Nonius Kappa CCD area detector (ϕ scans and ω scans to fill Ewald sphere). **Cell determination**: DirAx (Duisenberg, A.J.M. (1992). J. Appl. Cryst. 25, 92-96) **Data collections**: Collect: Data collections software R. Hooft, Nonius B. V., 1998). **Data reduction and cell refinement**: Denzo (Z. Otwinowski & W. Minor, Methods in Enzymology (1997) Vol. **276**: Macromolecular Crystallography, part A, pp. 307 – 326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: SORTAV (R. H. Blessing, Acta Cryst. A**51** (1995) 33-37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421-426). **Structure solution**: SHELXS97 (G. M.

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Special details: All Hydrogen atoms were placed in idealised positions and refined using a riding model.

Table 2. Atomic coordinates [x 10^4], equivalent isotropic displacement parameters [$\oplus^2$ x 10^3] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U_{eq}	S.o.f.
C1	789(1)	7320(5)	13333(2)	30(1)	1
C2	1041(1)	7512(5)	12788(2)	26(1)	1
C3	1320(1)	6723(5)	13153(2)	26(1)	1
C4	1593(1)	7036(5)	12724(2)	23(1)	1
C5	1860(1)	6414(5)	13047(3)	29(1)	1
C6	2114(1)	6715(5)	12685(3)	34(1)	1
C7	2114(1)	6771(5)	11987(3)	33(2)	1
C8	1854(1)	8285(5)	11649(3)	31(1)	1
C9	1599(1)	7964(5)	12019(2)	27(1)	1
C10	513(1)	13262(5)	11839(3)	45(1)	1
C11	759(2)	13062(6)	11312(3)	62(2)	1
C12	978(1)	11751(5)	11469(3)	48(2)	1
C13	1275(1)	12068(5)	11159(3)	32(1)	1
C14	1370(1)	11283(5)	10467(3)	33(1)	1
C15	1641(1)	11574(5)	10204(2)	33(2)	1
C16	1833(1)	12661(5)	10626(3)	31(2)	1
C17	1741(1)	13464(5)	11301(2)	30(1)	1
C18	1467(1)	13148(5)	11557(3)	33(2)	1
C19	265(1)	7365(5)	10357(2)	30(1)	1
C20	588(1)	7702(5)	10238(2)	35(2)	1
C21	704(1)	6696(5)	9546(2)	31(1)	1
C22	1017(1)	7018(5)	9411(2)	24(1)	1
C23	1244(1)	6269(5)	9877(3)	33(2)	1
C24	1530(1)	6578(5)	9754(2)	30(1)	1
C25	1606(1)	7652(5)	9135(3)	26(1)	1
C26	1384(1)	8408(5)	8664(3)	26(1)	1
C27	1099(1)	8100(5)	8808(2)	27(1)	1
C28	2388(1)	8885(5)	10948(3)	43(2)	1
C29	2305(1)	13902(6)	10766(3)	50(2)	1
C30	1979(1)	8869(5)	8388(3)	38(1)	1
01	324(1)	7459(3)	12087(1)	23(1)	1
02	471(1)	10254(3)	12786(2)	28(1)	1
03	207(1)	10263(3)	11335(1)	29(1)	1
04	0	12111(4)	12500	33(1)	1

05	-203(1)	7941(3)	11375(2)	29(1)	1
06	2381(1)	7931(4)	11678(2)	40(1)	1
07	2099(1)	12856(4)	10322(2)	43(1)	1
08	1896(1)	7867(3)	9054(2)	35(1)	1
Si1	143(1)	8268(1)	11293(1)	26(1)	1
Si2	441(1)	8256(1)	12955(1)	26(1)	1
Si3	296(1)	11451(1)	12116(1)	29(1)	1

Table 3. Bond lengths [⊕] and angles [°].

C1-C2	1.521(6)	C20-C21	1.524(5)
C1-Si2	1.836(5)	C21-C22	1.494(6)
C2-C3	1.521(6)	C22-C23	1.392(7)
C3-C4	1.504(6)	C22-C27	1.393(5)
C4-C9	1.384(5)	C23-C24	1.369(7)
C4-C5	1.397(7)	C24-C25	1.398(6)
C5-C6	1.368(7)	C25-O8	1.360(6)
C6-C7	1.385(6)	C25-C26	1.383(7)
C7-C8	1.378(7)	C26-C27	1.368(7)
C7-O6	1.377(6)	C28-O6	1.430(5)
C8-C9	1.380(7)	C29-O7	1.433(6)
C10-C11	1.479(7)	C30-O8	1.435(5)
C10-Si3	1.840(5)	O1-Si2	1.629(3)
C11-C12	1.470(7)	O1-Si1	1.641(3)
C12-C13	1.511(7)	O2-Si3	1.636(3)
C13-C18	1.375(7)	O2-Si2	1.637(3)
C13-C14	1.401(6)	O3-Si1	1.631(3)
C14-C15	1.365(7)	O3-Si3	1.635(3)
C15-C16	1.396(7)	O4-Si3i	1.6276(17)
C16-O7	1.360(6)	O4-Si3	1.6276(17)
C16-C17	1.378(6)	O5-Si2i	1.627(3)
C17-C18	1.379(6)	O5-Si1	1.628(3)
C19-C20	1.533(6)	Si2-O5i	1.627(3)
C19-Si1	1.829(4)		
C2-C1-Si2	115.9(3)	C15-C14-C13	121.6(5)
C3-C2-C1	112.3(3)	C14-C15-C16	120.6(4)
C4-C3-C2	117.0(4)	O7-C16-C17	125.1(5)
C9-C4-C5	116.8(4)	O7-C16-C15	116.3(4)
C9-C4-C3	123.2(5)	C17-C16-C15	118.6(5)
C5-C4-C3	120.0(4)	C16-C17-C18	119.8(5)
C6-C5-C4	121.5(4)	C13-C18-C17	122.8(4)
C5-C6-C7	120.5(5)	C20-C19-Si1	113.1(3)
C8-C7-O6	124.6(4)	C21-C20-C19	113.1(4)
C8-C7-C6	119.3(5)	C22-C21-C20	114.1(4)
O6-C7-C6	116.1(5)	C23-C22-C27	115.9(5)
C7-C8-C9	119.6(4)	C23-C22-C21	122.5(4)
C8-C9-C4	122.4(5)	C27-C22-C21	121.6(5)
C11-C10-Si3	120.5(3)	C24-C23-C22	122.2(4)
C12-C11-C10	121.0(4)	C23-C24-C25	120.5(5)
C11-C12-C13	116.4(4)	O8-C25-C26	125.6(4)
C18-C13-C14	116.6(5)	O8-C25-C24	116.2(5)
C18-C13-C12	120.8(4)	C26-C25-C24	118.2(5)
C14-C13-C12	122.6(5)	C27-C26-C25	120.2(4)
C26-C27-C22	123.0(5)	O1-Si1-C19	110.46(19)

Si2-O1-Si1	131.92(16)	O5i-Si2-O1	109.76(17)
Si3-O2-Si2	130.6(2)	O5i-Si2-O2	109.62(14)
Si1-O3-Si3	130.00(16)	O1-Si2-O2	105.18(14)
Si3i-O4-Si3	142.0(2)	O5i-Si2-C1	108.32(18)
Si2i-O5-Si1	137.5(2)	O1-Si2-C1	111.54(17)
C7-O6-C28	117.6(4)	O2-Si2-C1	112.38(19)
C16-O7-C29	117.4(4)	O4-Si3-O2	108.35(13)
C25-O8-C30	117.4(4)	O4-Si3-O3	108.96(15)
O5-Si1-O3	109.25(16)	O2-Si3-O3	106.01(14)
O5-Si1-O1	108.58(15)	O4-Si3-C10	108.7(2)
O3-Si1-O1	105.97(15)	O2-Si3-C10	112,5(2)
O5-Si1-C19	111.2(2)	O3-Si3-C10	112.24(18)
O3-Si1-C19	111.18(17)		

Symmetry transformations used to generate equivalent atoms:

(i) –x,y,-z+5/2

Table 4. Anisotropic displacement parameters [$\oplus^2$ x 10^3]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U^{11} + \ldots + 2hka^*b^*U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	23(4)	34(2)	33(3)	0(2)	4(3)	1(2)
C2	14(4)	31(2)	33(2)	-1(2)	4(2)	0(2)
C3	18(4)	32(2)	28(2)	1(2)	-1(2)	6(3)
C4	14(4)	25(2)	29(2)	-4(2)	4(3)	-1(2)
C5	26(5)	32(2)	31(3)	6(2)	3(3)	3(3)
C6	22(5)	35(2)	46(3)	4(2)	0(3)	10(3)
C7	24(5)	34(2)	42(3)	-2(2)	13(3)	2(3)
C8	23(5)	33(2)	37(3)	3(2)	9(3)	2(3)
C9	13(4)	35(2)	31(2)	2(2)	0(2)	9(2)
C10	46(2)	42(2)	49(2)	2(2)	13(2)	-2(2)
C11	57(3)	59(2)	71(2)	13(2)	13(2)	-6(2)
C12	32(5)	42(3)	71(4)	-9(2)	18(3)	-4(3)
C13	29(5)	30(2)	38(3)	1(2)	13(3)	-2(3)
C14	34(5)	27(2)	38(3)	-2(2)	0(3)	-7(3)
C15	35(5)	36(2)	29(3)	-1(2)	10(3)	-3(3)
C16	28(5)	28(2)	39(3)	7(2)	10(3)	2(3)
C17	22(5)	31(2)	36(3)	-2(2)	5(3)	-6(2)
C18	34(5)	31(2)	34(3)	-6(2)	11(3)	-8(3)
C19	13(4)	38(2)	39(3)	0(2)	7(3)	1(2)
C20	36(5)	36(2)	33(2)	-5(2)	16(3)	0(3)
C21	24(4)	38(2)	32(2)	-7(2)	9(3)	0(3)
C22	12(4)	31(2)	30(2)	-7(2)	3(3)	1(2)
C23	36(5)	34(2)	29(2)	5(2)	9(3)	-2(3)
C24	22(5)	34(2)	33(2)	7(2)	-1(3)	10(3)
C25	15(5)	30(2)	35(3)	-5(2)	7(3)	2(3)
C26	15(4)	33(2)	32(2)	5(2)	7(3)	2(3)
C27	17(4)	35(2)	30(2)	2(2)	2(3)	9(3)
C28	32(5)	51(3)	47(3)	5(2)	18(3)	-6(3)
C29	30(5)	48(3)	72(4)	-1(3)	12(3)	-8(3)
C30	15(4)	48(3)	52(3)	8(2)	14(3)	1(3)
O1	14(3)	25(1)	30(2)	1(1)	6(2)	1(1)
O2	17(3)	29(1)	39(2)	-3(1)	5(2)	-4(2)
O3	24(3)	30(2)	33(2)	6(1)	7(2)	4(2)
O4	31(4)	27(2)	43(2)	0	18(2)	0
O5	15(3)	40(2)	31(2)	-1(1)	7(2)	2(2)

O6	16(3)	51(2)	54(2)	8(2)	10(2)	5(2)
O7	22(3)	43(2)	66(2)	-9(2)	19(2)	-5(2)
O8	20(3)	39(2)	46(2)	7(1)	3(2)	5(2)
Si1	22(1)	29(1)	29(1)	-1(1)	10(1)	2(1)
Si2	20(1)	30(1)	30(1)	-1(1)	7(1)	-1(1)
Si3	24(1)	25(1)	39(1)	1(1)	13(1)	-1(1)

Table 5. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$\oplus^2$ x 10^3].

Atom	x	y	z	U_{eq}	S.o.f.
H1A	847	7819	13868	36	1
H1B	756	6118	13421	36	1
H2A	987	6989	12256	31	1
H2B	1075	8710	12694	31	1
H3A	1353	7125	13719	31	1
H3B	1289	5506	13178	31	1
H5	1865	5767	13529	35	1
H6	2292	6265	12914	41	1
H8	1849	8925	11164	37	1
H9	1421	8395	11781	32	1
H10A	377	14076	11572	54	1
H10B	592	13779	12352	54	1
H11A	673	12895	10751	75	1
H11B	864	14135	11316	75	1
H12A	901	10705	11222	58	1
H12B	1003	11572	12063	58	1
H14	1244	10530	10173	40	1
H15	1699	11031	9729	39	1
H17	1866	14233	11589	36	1
H18	1409	13701	12028	39	1
H19A	232	6148	10365	35	1
H19B	146	7827	9889	35	1
H20A	613	8901	10126	42	1
H20B	704	7434	10747	42	1
H21A	679	5498	9662	37	1
H21B	585	6953	9039	37	1
H23	1198	5518	10295	39	1
H24	1679	6059	10091	36	1
H26	1429	9144	8240	32	1
H27	950	8650	8482	33	1
H28A	2590	8977	10795	64	1
H28B	2310	9998	11038	64	1
H28C	2270	8332	10512	64	1
H29A	2487	13932	10489	74	1
H29B	2344	13460	11316	74	1
H29C	2226	15030	10796	74	1
H30A	2192	8920	8394	57	1
H30B	1901	9995	8440	57	1
H30C	1901	8377	7876	57	1

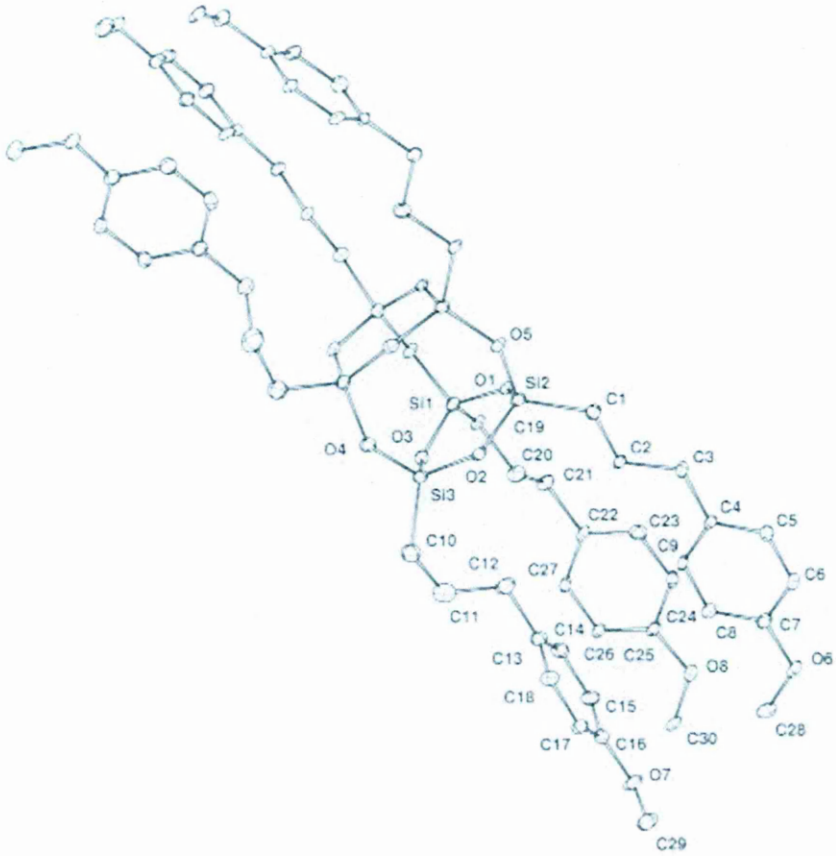
O5
O1
Si2
C1
Si1
C19
O3
C2
C3
O4
O2
C20
C21
Si3
C22
C23
C4
C5
C10
C9
C12
C27
C6
C11
C24
C8
C7
C14
C13
C26
C25
O8
O6
C18
C15
C17
C16
C30
C28
O7
C29

Figure 1.

A.2 - Crystal and structure refinement of *tert*-butyldisiloxanetetraol

Table 6.

Identification code	00src417	
Empirical formula	$C_8H_{22}O_5Si_2$	
Formula weight	254.44	
Temperature	150(2) K	
Wavelength	0.71073 ⊕	
Crystal System	Triclinic	
Space group	P-1	
Unit cell dimensions	a=6.2157(12) ⊕	α= 89.14(3)°
	b= 9.6972(19) ⊕	β= 79.65(3)°
	c= 11.921(2) ⊕	γ= 81.51(3)°
Volume	699.0(2) $⊕^3$	
Z	2	
Density (calculated)	1.209 Mg/m^3	
Absorption coefficient	0.254 mm^{-1}	
F (000)	276	
Crystal	Prism ; colourless	
Crystal size	0.20 x 0.12 x 0.12 mm^3	
Θ range for data collection	3.37 – 27.50°	
Index ranges	-7≤h ≤8, -12 ≤k ≤12 , -15≤l ≤15	
Reflections collected	9740	
Independent reflections	3090 [R_{int} = 0.0513]	
Completeness to Θ = 27.50°	96.7%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9701 and 0.9509	
Refinement method	Full-matrix least-squares on F^2	
Data/ restraints / parameters	3090/ 0 / 146	
Goodness-of-fit on F^2	0.998	
Final R indices [$F^2>2\sigma(F^2)$]	R1 = 0.0441 , wR2 = 0.1149	
R indices (all data)	R1 = 0.0599 , wR2 = 0.1251	
Largest diff. peak and hole	0.371 and –0.534 e $⊕^{-3}$	

Diffractometer: Enraf Nonius Kappa CCD area detector (ϕ scans and ω scans to fill Ewald sphere). **Data collection and cell refinement**: Denzo (Z. Otwinowski & W. Minor, Methods in Enzymology (1997) Vol. **276**: Macromolecular Crystallography, part A , pp. 307 – 326 ; C. W. Carter , Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: SORTAV (R. H. Blessing, Acta Cryst. A**51** (1995) 33-37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421-426). **Program used to solve structure**: SHELXS97 (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467-473). **Program used to refine structure**: SHELXL97 (G. M. Sheldrick (1997), University of Gottingen, Germany). **Further information:** http://www.soton.ac.uk/~xservice/strat.htm

Table 7. Atomic coordinates [x 10^4], equivalent isotropic displacement parameters [$\oplus^2$ x 10^3] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U_{eq}	S.o.f.
Si1	1351(1)	5598(1)	6539(1)	18(1)	1
Si2	3732(1)	4232(1)	8533(1)	17(1)	1
O1	2811(2)	5061(2)	5310(1)	26(1)	1
O2	2383(2)	4762(1)	7544(1)	25(1)	1
O3	5913(2)	5006(2)	8428(1)	25(1)	1
O4	2194(2)	4715(2)	9760(1)	25(1)	1
O5	-1081(2)	5165(2)	6545(1)	26(1)	1
C1	1231(3)	7498(2)	6745(2)	29(1)	1
C2	-77(4)	7947(3)	7932(2)	43(1)	1
C3	66(4)	8283(3)	5837(2)	45(1)	1
C4	3568(4)	7870(3)	6624(2)	43(1)	1
C5	4513(3)	2311(2)	8432(2)	29(1)	1
C6	2448(4)	1599(3)	8589(2)	44(1)	1
C7	5840(4)	1818(3)	9371(2)	43(1)	1
C8	5933(4)	1910(3)	7263(2)	46(1)	1

Table 8. Bond lengths [$\oplus$] and angles [°].

Si1-O2	1.6112(13)
Si1-O1	1.6269(14)
Si1-O5	1.6264(13)
Si1-C1	1.852(2)
Si2-O2	1.6023(12)
Si2-O3	1.6286(14)
Si2-O4	1.6301(14)
Si2-O5	1.854(2)
C1-C4	1.529(3)
C1-C2	1.534(3)
C1-C3	1.539(3)
C5-C6	1.527(3)
C5-C7	1.536(3)
C5-C8	1.531(3)
O2-Si1-O1	109.51(7)
O2-Si1-O5	108.05(7)
O1-Si1-O5	105.24(7)
O2-Si1-C1	110.02(9)
O1-Si1C1	111.75(9)
O5-Si1-C1	112.10(9)
O2-Si2-O3	109.60(7)
O2-Si2-O4	108.44(7)
O3-Si2-O4	106.35(7)
O2-Si2-C5	109.83(9)
O3-Si2-C5	111.00(9)
O4-Si2-C5	111.53(9)
Si2-O2-Si1	166.50(10)

C4-C1-C2	109.47(19)
C4-C1-C3	109.06(18)
C2-C1-C3	108.94(18)
C4-C1-Si1	110.14(15)
C2-C1-Si1	109.96(14)
C3-C1-Si1	109.26(16)
C6-C5-C7	108.80(18)
C6-C5-C8	109.42(19)
C7-C5-C8	109.35(18)
C6-C5-Si2	110.36(15)
C7-C5-Si2	109.36(16)
C8-C5-Si2	109.53(15)

Symmetry transformations used to generate equivalent atoms:

Table 9. Anisotropic displacement parameters [$\oplus^2$ x 10^3]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U^{11} + \ldots + 2hka^*b^*U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si1	12(1)	32(1)	10(1)	0(1)	-3(1)	-3(1)
Si2	13(1)	30(1)	10(1)	0(2)	-3(1)	-3(1)
O1	13(1)	49(1)	15(1)	-5(1)	0(1)	-4(1)
O2	24(1)	36(1)	17(1)	2(1)	-12(1)	-2(1)
O3	18(1)	43(1)	15(1)	1(1)	-1(1)	-11(1)
O4	18(1)	44(1)	13(1)	-3(1)	-2(1)	-4(1)
O5	15(1)	50(1)	16(1)	-1(1)	-2(1)	-10(1)
C1	26(1)	32(1)	26(1)	3(1)	1(1)	-2(1)
C2	50(2)	38(1)	36(1)	-9(1)	6(1)	-1(1)
C3	45(1)	42(1)	43(1)	16(1)	-3(1)	4(1)
C4	36(1)	39(1)	56(2)	-4(1)	-4(1)	-14(1)
C5	29(1)	32(1)	25(1)	1(1)	-1(1)	-2(1)
C6	48(2)	37(1)	47(1)	-2(1)	-5(1)	-15(1)
C7	42(1)	42(1)	42(1)	13(1)	-9(1)	5(1)
C8	51(2)	41(1)	38(1)	-10(1)	8(1)	6(1)

Table 10. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$\oplus^2$ x 10^3].

Atom	x	y	z	U_{eq}	S.o.f.
H1	4122	5201	5279	39	1
H3	6712	4830	7784	37	1
H4	2979	4639	10268	37	1
H5	-1830	5267	7207	40	1
H2A	-157	8956	8029	65	1
H2B	666	7461	8515	65	1
H2C	-1575	7710	8009	65	1
H3A	-1455	8081	5931	68	1
H3B	864	7979	5075	68	1
H3C	46	9288	5926	68	1
H4A	4403	7585	5865	65	1
H4B	4313	7383	7206	65	1

H4C	3487	8879	6722	65	1
H6A	2883	585	8555	66	1
H6B	1609	1887	7982	66	1
H6C	1525	1868	9332	66	1
H7A	4917	2047	10120	65	1
H7B	7153	2286	9288	65	1
H7C	6298	807	9302	65	1
H8A	6358	895	7214	69	1
H8B	7266	2360	7164	69	1
H8C	5085	2217	6663	69	1

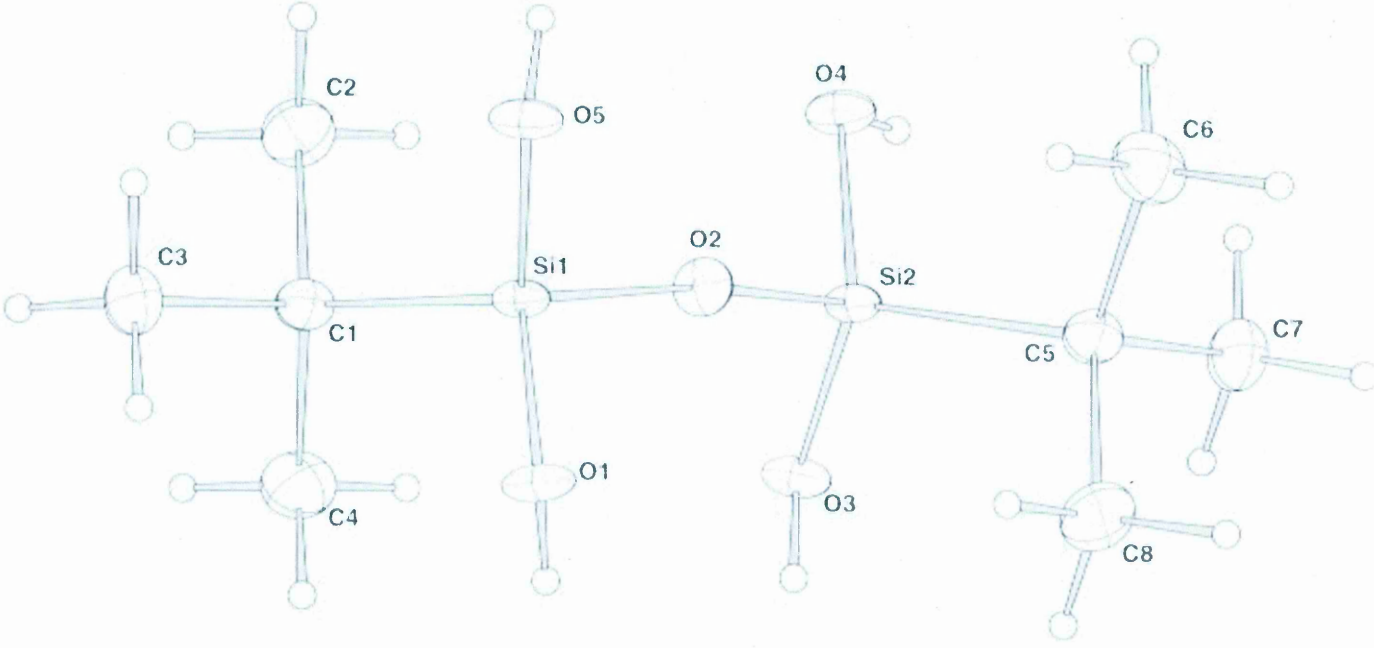

Figure 2.

A.3 - Crystal and structure refinement of cyclohexyltrimethylsilyl-cyclotetrasiloxane

Table 11. Crystal and structure refinement.

Identification code	01src440	
Empirical formula	$C_{36}H_{80}O_8Si_8$	
Formula weight	865.72	
Temperature	120(2) K	
Wavelength	0.71073 ⊕	
Crystal System	Triclinic	
Space group	P-1	
Unit cell dimensions	a=11.009(2) ⊕	α= 86.39(3)°
	b= 13.700(3) ⊕	β= 85.31(3)°
	c= 17.918(4) ⊕	γ= 75.39(3)°
Volume	2603.7(9) $⊕^3$	
Z	2	
Density (calculated)	1.104 Mg/m^3	
Absorption coefficient	0.246 mm^{-1}	
F (000)	944	
Crystal	Block ; colourless	
Crystal size	0.14 x 0.10 x 0.06 mm^3	
Θ range for data collection	2.94 – 27.50°	
Index ranges	-14≤h ≤14, -17 ≤k ≤17 , -22≤l ≤23	
Reflections collected	40144	
Independent reflections	11743 [R_{int} = 0.0593]	
Completeness to Θ = 27.50°	98.1%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9854 and 0.9664	
Refinement method	Full-matrix least-squares on F^2	
Data/ restraints / parameters	11743/ 18 / 482	
Goodness-of-fit on F^2	10052	
Final R indices [$F^2>2\sigma(F^2)$]	R1 = 0.0564 , wR2 = 0.1456	
R indices (all data)	R1 = 0.0774 , wR2 = 0.1620	
Extinction coefficient	0.0032(11)	
Largest diff. peak and hole	1.354 and –0.740 e $⊕^{-3}$	

Diffractometer: Enraf Nonius Kappa CCD area detector (ϕ scans and ω scans to fill Ewald sphere). **Data collection and cell refinement**: Denzo (Z. Otwinowski & W. Minor, Methods in Enzymology (1997) Vol. **276** : Macromolecular Crystallography , part A , pp. 307 – 326 ; C. W. Carter , Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: SORTAV (R. H. Blessing, Acta Cryst. A**51** (1995) 33-37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421-426). **Program used to solve structure**: SHELXS97 (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467-473). **Program used to**

refine structure: SHELXL97 (G. M. Sheldrick (1997), University of Gottingen, Germany). **Further information:** http://www.soton.ac.uk/~xservice/strat.htm

Table12. Atomic coordinates [x 10^4] , equivalent isotropic displacement parameters [$\oplus^2$ x 10^3] and site occupancy factors . U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U_{eq}	S.o.f.
C1	7679(4)	11246(3)	3127(2)	78(1)	1
C2	7653(3)	10427(3)	1611(2)	62(1)	1
C3	9908(3)	11161(2)	1968(2)	68(1)	1
C4	3241(3)	9054(3)	21902)	70(1)	1
C5	2634(3)	10239(2)	3600(2)	48(1)	1
C6	3782(4)	11152(3)	2222(2)	74(1)	1
C7	4604(3)	8469(4)	-22(2)	88(2)	1
C8	6630(5)	6536(3)	-261(3)	86(1)	1
C9	7300(3)	8420(3)	165(2)	63(1)	1
C10	10891(4)	8555(3)	472(3)	71(1)	1
C11	10992(5)	6712(4)	-426(3)	95(1)	1
C12	12735(5)	6505(4)	778(3)	108(2)	1
C13	5702(2)	7877(2)	4138(1)	32(1)	1
C14	6606(3)	6860(2)	4346(2)	44(1)	1
C15	6249(4)	6446(3)	5122(2)	63(1)	1
C16	6168(4)	7210(3)	5713(2)	64(1)	1
C17	5222(3)	8197(3)	5523(2)	53(1)	1
C18	5578(3)	8629(2)	4755(1)	38(1)	1
C19	6054(3)	5686(2)	2245(2)	40(1)	1
C20	4733(3)	5882(2)	2634(2)	52(1)	1
C21	4401(4)	4896(3)	2920(2)	71(1)	1
C22	4555(4)	4172(3)	2292(2)	68(1)	1
C23	5863(4)	3960(2)	1913(2)	71(1)	1
C24	6194(3)	4944(2)	1615(2)	51(1)	1
C25	9889(2)	7900(2)	3862(1)	32(1)	1
C26	9694(3)	8666(2)	4474(2)	41(1)	1
C27	10328(3)	8188(2)	5181(2)	49(1)	1
C28	11725(3)	7711(3)	5020(2)	53(1)	1
C29	11948(3)	6957(2)	4401(2)	51(1)	1
C30	11310(2)	7441(2)	3694(2)	41(1)	1
C31	10334(2)	5435(2)	2322(1)	33(1)	1
C32	9782(3)	5236(2)	3116(1)	40(1)	1
C33	10530(3)	4248(2)	3476(2)	54(1)	1
C34	10599(3)	3356(2)	2992(2)	53(1)	1
C35	11151(3)	3538(2)	2202(2)	45(1)	1
C36	10419(3)	4527(2)	1840(2)	39(1)	1
O1	6192(2)	7644(1)	2565(1)	35(1)	1
O2	8061(2)	6546(1)	1730(1)	34(1)	1
O3	9385(2)	7564(1)	2385(1)	35(1)	1
O4	7520(2)	8646(1)	2339(1)	33(1)	1
O5	9377(2)	9420(1)	2863(1)	38(1)	1
O6	5164(2)	9475(1)	3020(1)	36(1)	1
O7	5875(2)	7347(1)	1169(1)	35(1)	1
O8	10117(2)	6824(2)	1058(1)	47(1)	1

Si1	6154(1)	8418(1)	3213(1)	26(1)	1
Si2	6552(1)	6840(1)	1915(1)	28(1)	1
Si3	9024(1)	8395(1)	3019(1)	30(1)	1
Si4	9460(1)	6628(1)	1868(1)	29(1)	1
Si5	8660(1)	10543(1)	2356(1)	34(1)	1
Si6	3732(1)	9968(1)	2757(1)	39(1)	1
Si7	11178(1)	7162(1)	497(1)	42(1)	1
Si8	6113(1)	7679(1)	284(1)	37(1)	1

Table 13. Bond lengths [⊕] and angles [°].

C1-Si5	1.845(4)
C2-Si5	1.842(3)
C3-Si5	1.855(3)
C4-Si6	1.867(4)
C5-Si6	1.851(3)
C6-Si6	1.843(3)
C7-Si8	1.844(4)
C8-Si8	1.839(5)
C9-Si8	1.838(3)
C10-Si7	1.853(3)
C11-Si7	1.845(5)
C12-Si7	1.818(5)
C13-C18	1.534(3)
C13-C14	1.539(4)
C13-Si1	1.853(2)
C14-C15	1.527(4)
C15-C16	1.517(5)
C16-C17	1.522(5)
C17-C18	1.524(4)
C19-C20	1.528(4)
C19-C24	1.538(4)
C19-Si2	1.849(3)
C20-C21	1.533(4)
C21-C22	1.519(5)
C22-C23	1.507(6)
C23-C24	1.537(4)
C25-C26	1.531(4)
C25-C30	1.544(3)
C25-Si3	1.852(3)
C26-C27	1.527(4)
C27-C28	1.523(4)
C28-C29	1.526(4)
C29-C30	1.531(4)
C31-C32	1.537(4)
C31-C36	1.538(3)
C31-Si4	1.851(2)
C32-C33	1.530(4)
C33-C34	1.526(4)
C34-C35	1.525(4)
C35-C36	1.526(4)
O1-Si2	1.6094(17)
O1-Si1	1.6126(17)
O2-Si4	1.6131(18)
O2-Si2	1.6188(18)
O3-Si4	1.6110(18)

O3-Si3	1.6132(18)
O4-Si1	1.6164(17)
O4-Si3	1.6238(18)
O5-Si3	1.6177(17)
O5-Si5	1.6388(19)
O6-Si1	1.6141(18)
O6-Si6	1.6462(19)
O7-Si2	1.6150(18)
O7-Si8	1.6404(18)
O8-Si4	1.6050(19)
O8Si7	1.616(2)
C18-C13-C14	110.8(2)
C18-C13-Si1	111.13(17)
C14-C13-Si1	112.71(17)
C15-C14-C13	112.0(3)
C16-C15-C14	111.1(3)
C15-C16-C17	110.8(3)
C16-C17-C18	110.6(3)
C17-C18-C13	112.1(2)
C20-C19-C24	110.5(2)
C20-C19-Si2	114.4(2)
C24-C19-Si2	112.08(18)
C19-C20-C21	111.7(3)
C22-C21-C20	111.1(3)
C23-C22-C21	111.6(3)
C22-C23-C24	111.0(3)
C23-C24-C19	111.2(3)
C26-C25-C30	109.7(2)
C26-C25-Si3	113.73(17)
C30-C25-Si3	114.04(18)
C27-C26-C25	111.3(2)
C28-C27-C26	111.9(2)
C27-C28-C29	111.4(2)
C28-C29-C30	111.3(2)
C29-C30-C25	111.5(2)
C32-C31-C36	109.9(2)
C32-C31-Si4	113.07(17)
C36-C31-Si4	111.53(17)
C33-C32-C31	111.7(2)
C34-C33-C32	111.3(2)
C35-C34-C33	110.9(2)
C34-C35-C36	111.5(2)
C35-C36-C31	112.3(2)
Si2-O1-Si1	167.71(12)
Si4-O2-Si2	152.01(12)
Si4-O3-Si3	165.25(13)
Si1-O4-Si3	151.85(12)
Si3-O5-Si5	138.58(12)
Si1-O6-Si6	143.13(12)
Si2-O7-Si8	144.63(12)
Si4-O8-Si7	154.05(16)
O1-Si1-O6	109.13(10)
O1-Si1-O4	109.89(10)
O6-Si1-O4	107.56(9)
O1-Si1-C13	110.33(10)
O6-Si1-C13	110.53(11)
O4-Si1-C13	109.36(11)

O1-Si2-O7	108.94(10)
O1-Si2-O2	109.51(10)
O7-Si2-O2	108.93(9)
O1-Si2-C19	109.18(11)
O7-Si2-C19	111.50(11)
O2-Si2-C19	108.76(12)
O3-Si3-O5	108.91(10)
O3-Si3-O4	109.47(10)
O5-Si3-O4	108.55(10)
O3-Si3-C25	109.65(10)
O5-Si3-C25	110.68(11)
O4-Si3-C25	109.57(10)
O8-Si4-O3	109.68(11)
O8-Si4-O2	106.51(11)
O3-Si4-O2	109.87(10)
O8-Si4-C31	110.90(11)
O3-Si4-C31	110.35(11)
O2-Si4-C31	109.46(11)
O5-Si5-C2	109.98(15)
O5-Si5-C1	108.75(14)
C2-Si5-C1	109.43(19)
O5-Si5-C3	106.63(13)
C2-Si5-C3	110.09(17)
C1-Si5-C3	111.9(2)
O6-Si6-C6	106.43(15)
O6-Si6-C5	109.05(12)
C6-Si6-C5	110.04(16)
O6-Si6-C4	109.75(13)
C6-Si6-C4	112.5(2)
C5-Si6-C4	109.02(16)
O8-Si7-C12	109.79(19)
O8-Si7-C11	105.20(19)
C12-Si7-C11	107.6(2)
O8-Si7-C10	109.24(15)
C12-Si7-C10	113.5(2)
C11-Si7-C10	111.2(2)
O7-Si8-C9	110.94(13)
O7-Si8-C8	108.99(16)
C9-Si8-C8	110.2(2)
O7-Si8-C7	107.06(14)
C9-Si8-C7	108.96(19)
C8-Si8-C7	110.7(2)

Symmetry transformations used to generate equivalent atoms:

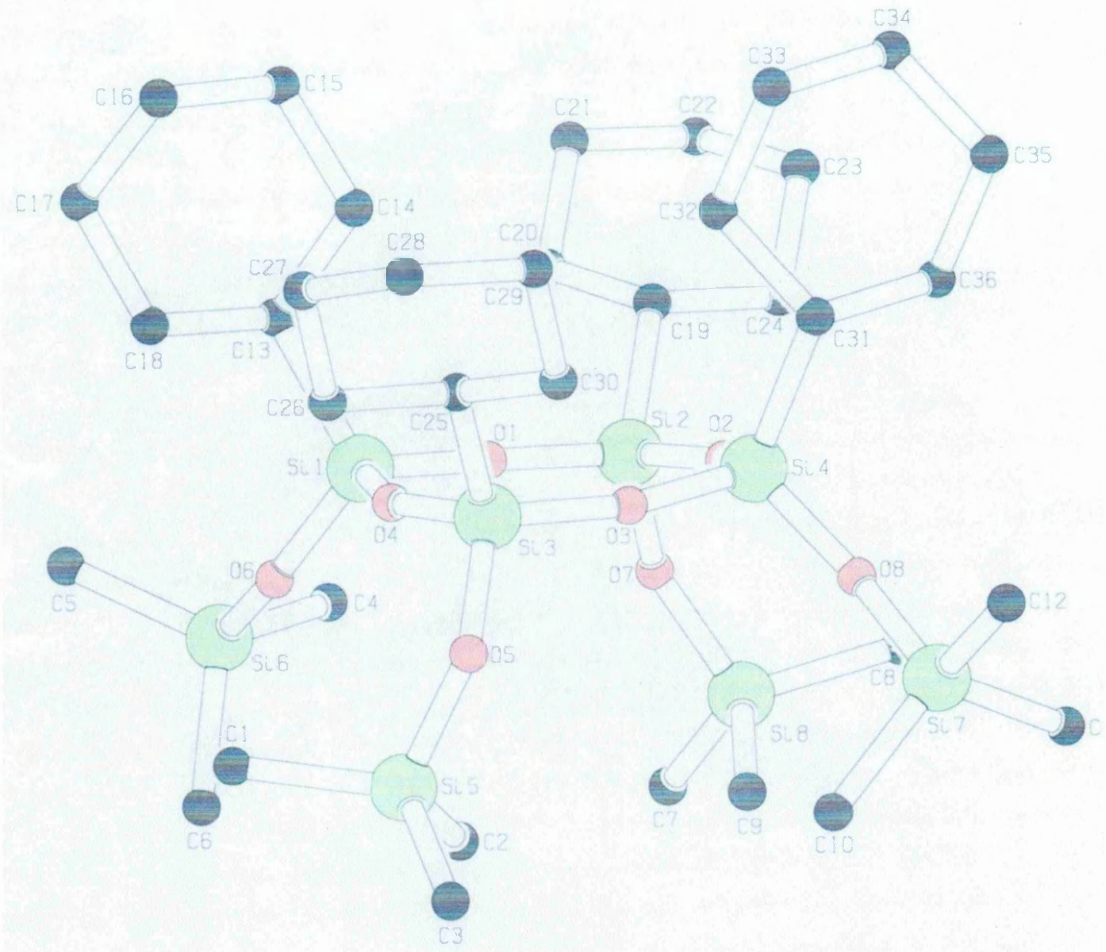
C34
C33
C16
C15
C21
C22
C35
C23
C17
C14
C32
C28
C20
C27
C29
C36
C18
C13
C19
C24
C31
C30
C26
C25
O1
Si2
O2
Si1
Si4
O4
Si3
O3
O6
O7
O8
C12
C5
C4
Si6
O5
C8
C1
Si8
Si7
C
Si5
C7
C9
C10
C6
C2
C3

Figure 3.

A. 4 - Crystal and structure refinement of cyclohexyl sodium siloxysilanolate. Table 14

Identification code	00src612	
Compound	$Na_6(Si_3O6_8C_{18}H_{33})_2 \bullet 18H_20$	
Empirical formula	$C_{36}H_{102}Na_6O_{30}Si_6$	
Formula weight	1321.66	
Temperature	150(2) K	
Wavelength	0.71073 ⊕	
Crystal System	Triclinic	
Space group	P-1	
Unit cell dimensions	a=9.16150(10) ⊕	α= 88.5860(10)°
	b= 10.1143(2) ⊕	β= 80.2380(10)°
	c= 18.1371(5) ⊕	γ= 70.995(2)°
Volume	1565.16(6) $⊕^3$	
Z	1	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	0.256 mm^{-1}	
F (000)	708	
Crystal	Block ; colourless	
Crystal size	0.15 x 0.10 x 0.10 mm^3	
Θ range for data collection	3.00 – 26.00°	
Index ranges	-10≤h ≤11, -12 ≤k ≤12 , -16≤l ≤22	
Reflections collected	10149	
Independent reflections	7727 [R_{int} = 0.0314]	
Completeness to Θ = 26.00°	95.8%	
Max. and min. transmission	0.9748 and 0.9626	
Refinement method	Full-matrix least-squares on F^2	
Data/ restraints / parameters	7727/ 3 / 759	
Goodness-of-fit on F^2	0.935	
Final R indices [$F^2 > 2\sigma(F^2)$]	R1 = 0.0338 , wR2 = 0.0866	
R indices (all data)	R1 = 0.0389 , wR2 = 0.0895	
Absolute structure parameter	0.28(10)	
Extinction coefficient	0.0026(9)	
Largest diff. peak and hole	0.324 and –0.337 e $⊕^{-3}$	

Diffractometer: Enraf Nonius Kappa CCD area detector (ϕ scans and ω scans to fill Ewald sphere). **Data collection and cell refinement**: Denzo (Z. Otwinowski & W. Minor, Methods in Enzymology (1997) Vol. **276**: Macromolecular Crystallography, part A, pp. 307 – 326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: SORTAV (R. H. Blessing, Acta Cryst. A**51** (1995) 33-37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421-426). **Program used to solve structure**: SHELXS97 (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467-473). **Program used to**

refine structure: SHELXL97 (G. M. Sheldrick (1997), University of Gottingen, Germany). **Further information:** http://www.soton.ac.uk/~xservice/strat.htm

Special detail:

The asymmetric unit contains two $Si_3O_6C_{18}H_{33}$ molecules, 6 Na and 18 H_2O. The arrangement of the two independent $Si_3O_6C_{18}H_{33}$ molecules shows approximate inversion symmetry. These molecules are arranged in chains that extend along the crystallographic *a* and *b* axes, with their oxo-O's face-to-face. They are connected to the polymeric $nNa.3nH_2O$ core via O4 and O3 (molecule 1) and O7, O8, O9, O11, O12 (molecule 2). Thus, the molecules are infinite 2D-networks that extend parallel to the crystallographic (001) plane. The two "surfaces" of each plane are dominated by the cyclohexane groups. The coordination numbers of the Na atoms are Na1[6] , Na2[5+1] , Na3[6+1] , Na4[6+1] , Na5[6] and Na6[6] . The networks are supported by a number of hydrogen bonds (Table 5).

Due to the chemical content of the compound, the absolute structure cannot be determined reliably, the refined Flack-parameter might also suggest a racemic twin.

Table 15. Atomic coordinates [x 10^4], equivalent isotropic displacement parameters [$\oplus^2$ x 10^3] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U_{eq}	S.o.f.
Si1	1036(1)	9712(1)	4721(1)	11(1)	1
Si2	13889(1)	8692(1)	4519(1)	11(1)	1
Si3	12168(1)	6578(1)	4626(1)	11(1)	1
O1	9208(3)	10366(3)	5474(1)	13(1)	1
O2	12125(3)	9863(3)	4680(1)	15(1)	1
O3	14979(3)	8920(3)	5065(1)	16(1)	1
O4	13640(3)	7152(3)	4698(1)	13(1)	1
O5	11975(3)	5568(3)	5295(1)	14(1)	1
O6	10639(3)	8021(3)	4659(1)	13(1)	1
C10	9553(4)	10550(4)	3882(2)	16(1)	1
C11	10277(5)	9800(5)	3132(2)	26(1)	1
C12	9462(5)	10566(5)	2502(2)	27(1)	1
C13	9460(5)	12064(5)	2465(2)	29(1)	1
C14	8749(6)	12830(5)	3220(2)	38(1)	1
C15	9574(6)	12076(5)	3836(2)	33(1)	1
C20	14706(4)	8616(4)	3499(2)	14(1)	1
C21	15084(5)	9901(4)	3187(2)	21(1)	1
C22	15540(6)	9780(5)	2340(2)	30(1)	1
C23	16898(6)	8456(5)	2090(2)	32(1)	1
C24	16584(5)	7141(5)	2409(2)	28(1)	1
C25	16116(5)	7298(4)	3262(2)	22(1)	1
C30	12560(4)	5767(4)	3672(2)	13(1)	1
C31	11146(4)	5525(4)	3421(2)	20(1)	1
C32	11552(5)	5007(5)	2602(2)	29(1)	1
C33	12960(5)	3677(5)	2475(2)	28(1)	1
C34	14377(5)	3859(5)	2479(2)	30(1)	1
C35	13948(5)	4399(4)	3566(2)	20(1)	1
Si4	7746(1)	9691(1)	8571(1)	11(1)	1
Si5	5590(1)	7613(1)	8622(1)	11(1)	1
Si6	9498(1)	6537(1)	8487(1)	11(1)	1
O7	8063(3)	10706(3)	7927(1)	15(1)	1
O8	6303(3)	9121(3)	8437(1)	12(1)	1
O9	4998(3)	7363(3)	8034(1)	15(1)	1
O10	7745(3)	6410(3)	8511(1)	13(1)	1
O11	10654(3)	5924(3)	7720(1)	14(1)	1
O12	9255(3)	8240(4)	8557(1)	13(1)	1
C40	7270(4)	10492(4)	9530(2)	15(1)	1
C41	5892(4)	11873(4)	9620(2)	19(1)	1
C42	5429(5)	1243(5)	10424(2)	26(1)	1
C43	6819(5)	12629(5)	10705(2)	28(1)	1
C44	8222(5)	11278(5)	10613(2)	24(1)	1
C45	8670(4)	10716(4)	9806(2)	18(1)	1
C50	5093(4)	7727(4)	9626(2)	14(1)	1
C51	3666(4)	9025(4)	9863(2)	20(1)	1
C52	3166(5)	9156(5)	10719(2)	27(1)	1
C53	2840(5)	7860(5)	11031(2)	32(1)	1
C54	4235(5)	6548(5)	10786(2)	30(1)	1
C55	4730(5)	6413(5)	9925(2)	22(1)	1
C60	10315(4)	5646(4)	9307(2)	15(1)	1
C61	9551(5)	6400(5)	10078(2)	23(1)	1
C62	10354(5)	5606(5)	10705(2)	26(1)	1
C63	10368(5)	4104(5)	10725(2)	25(1)	1
C64	11097(5)	3345(5)	9978(2)	29(1)	1
C65	10284(5)	4158(4)	9345(2)	24(1)	1
Na1	20021(2)	3106(2)	6594(1)	16(1)	1
Na2	5583(2)	9329(2)	7203(1)	27(1)	1
Na3	10488(2)	8331(2)	7203(1)	20(1)	1

Na4	15196(2)	6567(2)	5654(1)	22(1)	1
Na5	13959(2)	2169(2)	6264(1)	17(1)	1
Na6	16025(2)	3951(2)	6880(1)	18(1)	1
O13	19616(3)	5551(3)	6458(1)	16(1)	1
O14	21966(3)	3203(3)	7263(1)	17(1)	1
O15	17964(3)	3555(3)	7702(1)	19(1)	1
O16	21999(3)	2760(3)	5474(2)	23(1)	1
O17	1790(3)	7414(3)	5106(2)	26(1)	1
O18	1750(3)	5072(3)	4811(2)	29(1)	1
O19	14670(3)	4159(3)	5762(2)	21(1)	1
O20	16396(3)	6192(3)	6683(1)	16(1)	1
O21	12690(3)	6958(3)	6419(1)	21(1)	1
O22	12050(3)	8818(3)	8054(2)	23(1)	1
O23	20349(3)	648(3)	6735(1)	16(1)	1
O24	18111(3)	3063(3)	5898(1)	17(1)	1
O25	3729(3)	9933(3)	6452(1)	18(1)	1
O26	8253(3)	8668(3)	6529(1)	22(1)	1
O27	16021(3)	1196(3)	5271(2)	23(1)	1
O28	15618(3)	1777(3)	7263(2)	29(1)	1
O29	13828(3)	5262(3)	7692(2)	27(1)	1
O30	2882(4)	11090(3)	8230(2)	36(1)	1

Table 16. Bond lengths [⊕] and angles [°].

Si1-O1	1.590(3)
Si1-O6	1.649(3)
Si1-O2	1.656(2)
Si1-C10	1.870(4)
Si2-O3	1.590(3)
Si2-O2	1.646(3)
Si2-O4	1.664(3)
Si2-C20	1.868(4)
Si3-O5	1.590(3)
Si3-O6	1.655(3)
Si3-O4	1.657(2)
Si3-C30	1.861(4)
O3-Na4	2.546(3)
O4-Na4	2.372(3)
C10-C11	1.511(5)
C10-C15	1.550(6)
C11-C12	1.528(6)
C12-C13	1.514(6)
C13-C14	1.524(6)
C14-C15	1.505(6)
C20-C21	1.523(5)
C21-C25	1533(5)
C21-C22	1.518(5)
C221-C23	1.517(5)
C23-C24	1.530(6)
C24-C25	1.531(6)
C25-C26	1.534(6)
C30-C31	1.534(5)
C31-C32	1.532(5)

C32-C33	1.520(5)
C33-C34	1.532(6)
C34-C35	1.533(6)
Si4-O7	1.588(5)
Si4-O12	1.653(3)
Si4-O8	1.658(3)
Si4-C40	1.859(2)
Si5-O9	1.586(4)
Si5-O10	1.654(3)
Si5-O8	1.658(3)
Si5-C50	1.856(3)
Si6-O11	1.599(4)
Si6-O10	1.645(3)
Si6-O12	1.668(2)
Si6-C60	1.859(3)
O7-Na3	2.850(4)
O8-Na2	2.424(3)
O9-Na2	2.605(3)
O11-Na3	2.554(3)
O12-Na3	2.536(3)
C40-C45	1.537(3)
C40-C41	1.537(5)
C41-C42	1.518(5)
C42-C43	1.519(5)
C43-C44	1.530(6)
C44-C45	1.523(6)
C50-C51	1.529(5)
C50-C55	1.537(5)
C51-C52	1.539(5)
C52-C53	1.512(6)
C53-C54	1.524(6)
C54-C55	1.546(5)
C60-C65	1.514(6)
C60-C61	1.548(5)
C61-C62	1.528(5)
C62-C63	1.514(6)
C63-C64	1.511(6)
C64-C65	1.547(5)
Na1-O24	2.336(3)
Na1-O14	2.347(3)
Na1-O13	2.391(3)
Na1-O23	2.417(3)
Na1-O16	2.431(3)
Na1-O15	2.455(3)
Na2-O25	2.276(3)
Na2-O26	2.426(3)
Na2-O28ii	2.491(3)
Na2-O30	2.915(4)
Na3-O21	2.306(3)
Na3-O22	2.431(3)
Na3-O23ii	2.444(3)
Na3-O26	2.486(3)
Na4-O20	2.285(3)
Na4-O21	2.389(3)
Na4-O18	2.454(3)
Na4-O19	2.629(3)
Na4-O17	2.893(3)
Na5-O14iii	2.332(3)

Na5-O27	2.345(3)
Na5-O25iv	2.350(3)
Na5-O16iii	2.401(3)
Na5-O19	2.422(3)
Na5-O28	2.502(3)
Na6-O29	2.309(3)
Na6-O24	2.332(3)
Na6-O20	2.409(3)
Na6-O28	2.414(3)
Na6-O15	2.431(3)
Na6-O19	2.522(3)
O14-Na5i	2.332(3)
O16-Na5i	2.401(3)
O23-Na3iv	2.444(3)
O25-Na5ii	2.350(3)
O28-Na2iv	2.491(3)
O1-Si1-O6	109.70(13)
O1-Si1-O2	112.93(13)
O6-Si1-O2	112.0(14)
O1-Si1-C10	106.28(15)
O6-Si1-C10	111.20(15)
O2-Si1-C10	108.36(15)
O3-Si2-O2	108.17(15)
O3-Si2-O4	111.99(14)
O2-Si2-O4	107.77(13)
O3-Si2-C20	105.91(15)
O2-Si2-C20	115.37(16)
O4-Si2-C20	109.43(15)
O5-Si3-O6	105.74(13)
O5-Si3-O4	113.21(13)
O6-Si3-O4	109.21(13)
O5-Si3-C30	104.12(15)
O6-Si3-C30	107.15(15)
O4-Si3-C30	107.46(15)
Si2-O2-Si1	131.47(17)
Si2-O3-Na4	91.61(12)
Si3-O4-Si2	131.54(17)
Si3-O4-Na4	125.21(13)
Si2-O4-Na4	96.13(12)
Si1-O6-Si3	135.03(15)
C11-C10-C15	109.4(3)
C11-C10-Si1	117.4(3)
C15-C10-Si1	110.2(3)
C10-C11-C12	111.9(4)
C13-C12-C11	111.5(3)
C12-C13-C14	110.7(3)
C15-C14-C13	111.7 (4)
C14-C15-C10	111.2(4)
C21-C20-C25	109.8(3)
C21-C20-Si2	116.7(3)
C25-C20-Si2	112.8(3)
C22-C21-C20	111.4(3)
C21-C22-C23	111.5(4)
C22-C23-C24	112.5(3)
C23-C24-C25	110.3(4)
C24-C25-C20	111.5(3)
C31-C30-C35	109.3(3)
C31-C30-Si3	115.1(3)

C35-C30-Si3	112.7(3)
C32-C31-C30	110.6(3)
C33-C32-C31	111.5(4)
C32-C33-C34	111.7(4)
C33-C34-C35	111.0(3)
C34-C35-C30	111.4(3)
O7-Si4-O12	112.07(13)
O7-Si4-O8	110.65(13)
O12-Si4-O8	103.62(13)
O7-Si4-C40	114.03(16)
O12-Si4-C40	107.31(16)
O8-Si4-C40	108.57(14)
O9-Si5-O10	110.99(14)
O9-Si5-O8	107.76(14)
O10-Si5-O8	105.63(13)
O9-Si5-C50	117.00(15)
O10-Si5-C50	108.45(16)
O8-Si5-C50	106.32(15)
O11-Si6-O10	112.60(13)
O11-Si6-O12	108.08(13)
O10-Si6-O12	106.60(13)
O11-Si6-C60	111.31(16)
O10-Si6-C60	108.81(15)
O12-Si6-C60	109.30(16)
O11-Si6-Na3	54.94(10)
O10-Si6-Na3	114.56(10)
O12-Si6-Na3	54.46(9)
C60-Si6-Na3	136.44(12)
Si4-O7-Na3	86.95(12)
Si5-O8-Si4	131.71(16)
Si5-O8-Na2	95.95(12)
Si4-O8-Na2	117.96(13)
Si5-O9-Na2	91.08(12)
Si6-O10-Si5	131.45(17)
Si6-O11-Na3	94.24(13)
Si4-O12-Si6	134.44(15)
Si4-O12-Na3	96.81(12)
Si6-O12-Na3	93.18(11)
C45-C40-C41	109.4(3)
C45-C40-Si4	114.1(2)
C41-C40-Si4	113.0(3)
C42-C41-C40	111.9(3)
C41-C42-C43	110.7(3)
C42-C43-C44	111.6(4)
C45-C44-C43	111.4(3)
C44-C45-C40	111.1(3)
C51-C50-C55	109.8(3)
C51-C50-Si5	115.1 (3)
C55-C50-Si5	115.2 (3)
C50-C51-C52	111.5 (3)
C53-C52-C51	111.5(4)
C52-C53-C54	111.1(3)
C53-C54-C55	112.0(4)
C50-C55-54	110.2(3)
C65-C60-C61	109.0(3)
C65-C60-Si6	111.3(3)
C61-C60-Si6	115.9(3)
C62-C61-C60	111.3(3)

C63-C62-C61	112.0(3)
C64-C63-C62	111.6(3)
C63-C64-C65	110.8(4)
C60-C65-C64	112.5(3)
O24-Na1-O14	177.96 (15)
O24-Na1-O13	94.87(11)
O14-Na1-O13	83.58 (10)
O24-Na1-O23	83.82 (10)
O14-Na1-O23	97.76(11)
O13-Na1-O23	178.34 (12)
O24-Na1-O16	91.91 (11)
O14-Na1-O16	86.67(10)
O13-Na1-O16	86.07(11)
O23-Na1-O16	94.98(12)
O24-Na1-O15	86.36(10)
O14-Na1-O15	95.06(11)
O13-Na1-O15	94.02(11)
O23-Na1-O15	84.89(10)
O16-Na1-O15	178.27(13)
O25-Na2-O8	150.58(11)
O25-Na2-O26	114.05(10)
O8-Na2-O26	95.19 (9)
O25-Na2-O28ii	91.77(11)
O8-Na2-O28ii	85.88(10)
O26-Na2-O28ii	87.95(10)
O25-Na2-O9	105.50(10)
O8-Na2-O9	62.69(9)
O26-Na2-O9	113.50(10)
O28ii-Na2-O9	142.40(11)
O25-Na2-O30	78.87(10)
O8-Na2-O30	72.96(9)
O26-Na2-O30	154.14(10)
O28ii-Na2-O30	68.70(10)
O9-Na2-O30	81.98(9)
O21-Na3-O22	92.08(10)
O21-Na3-O23ii	100.41(10)
O22-Na3-O23ii	84.46(10)
O21-Na3-O26	106.30(10)
O22-Na3-O26	159.21(11)
O23ii-Na3-O26	82.75(9)
O21-Na3-O12	135.39(10)
O22-Na3-O12	68.82(9)
O23ii-Na3-O12	116.44(10)
O26-Na3-O12	102.64(9)
O21-Na3-O11	80.03(9)
O22-Na3-O11	94.25(10)
O23ii-Na3-O11	178.64(11)
O26-Na3-O11	98.37(9)
O12-Na3-O11	62.61(9)
O21-Na3-O7	161.84(9)
O22-Na3-O7	84.74(9)
O23ii-Na3-O7	61.52(8)
O26-Na3-O7	74.76(8)
O12-Na3-O7	59.56(8)
O11-Na3-O7	117.99(9)
O20-Na4-O4	172.08(11)
O20-Na4-O21	91.30(10)
O4-Na4-O21	81.67(9)

O20-Na4-O18	94.44(11)
O4-Na4-O18	93.48(11)
O21-Na4-O18	151.26(11)
O20-Na4-O3	114.15(10)
O4-Na4-O3	64.50(9)
O21-Na4-O3	103.75(10)
O18-Na4-O3	99.49(10)
O20-Na4-O19	92.71(10)
O4-Na4-O19	88.64(10)
O21-Na4-O19	72.38(9)
O18-Na4-O19	79.23(10)
O3-Na4-O19	153.07(10)
O3-Na4-O17	79.60(9)
O4-Na4-O17	104.89(9)
O21-Na4-O17	151.27(11)
O18-Na4-O17	57.33(10)
O3-Na4-O17	57.33(8)
O19-Na4-O17	134.70(10)
O14iii-Na5-O27	177.47(12)
O14iii-Na5-O25iv	93.69(11)
O27-Na5-O25iv	88.38(11)
O14iii-Na5O16iii	87.72(10)
O27-Na5-O16iii	93.69(11)
O25iv-Na5-O16iii	91.52(11)
O14iii-Na5-O19	101.84(11)
O27-Na5-O19	76.15(10)
O25iv-Na5-O19	164.29(12)
O16iii-Na5-O19	86.81(10)
O14iii-Na5-O28	82.29(10)
O27-Na5-O28	96.28(11)
O25iv-Na5-O28	89.79(10)
O16iii-Na5-O28	169.98(12)
O19-Na5-O28	94.56(11)
O29-Na6-O24	167.29(13)
O29-Na6-O20	82.43(11)
O24-Na6-O20	87.41(10)
O29-Na6-O28	92.57(11)
O24-Na6-O28	98.34(11)
O20-Na6-O28	171.94(12)
O29-Na6-O15	100.10(11)
O24-Na6-O15	87.00(10)
O20-Na6-O15	87.48(10)
O28-Na6-O15	87.18(10)
O29-Na6-O19	95.53(11)
O24-Na6-O19	77.25(10)
O20-Na6-O19	92.54(10)
O28-Na6-O19	94.24(11)
O15-Na6-O19	164.24(11)
Na5i-O14-Na1	92.09(11)
Na6-O15-Na1	89.06(10)
Na5i-O16-Na1	88.38(11)
Na5-O19-Na6	84.79(10)
Na5-O19-Na4	162.31(13)
Na6-O19-Na4	82.30(9)
Na4-O20-Na6	92.44(10)
Na3-O21-Na4	152.55(12)
Na1-O23-Na3iv	165.93(13)
Na6-O24-Na1	94.46(11)

Na2-O25-Na5ii	92.64(10)
Na2-O26-Na3	120.91(10)
Na6-O28-Na2iv	160.50(15)
Na6-O28-Na5	85.40(10)
Na2iv-O28-Na5	84.17(10)

Symmetry transformations used to generate equivalent atoms:

(i) X+1,y,z (ii) x-1,y+1,z (iii) x-1,y,z (iv) x+1,y-1,z

Table 17. Anisotropic displacement parameters [$\oplus^2$ x 10^3]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U^{11} + \ldots + 2hka^*b^*U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si1	9(1)	11(1)	12(1)	0(1)	-2(1)	-2(1)
Si2	10(1)	12(1)	13(1)	0(1)	-2(1)	-4(1)
Si3	11(1)	9(1)	13(1)	1(1)	-2(1)	-3(1)
O1	12(1)	12(1)	15(1)	2(1)	-3(1)	-4(1)
O2	14(1)	14(2)	19(1)	3(1)	-6(1)	-6(1)
O3	13(1)	20(2)	19(1)	-4(1)	-5(1)	-8(1)
O4	12(1)	14(2)	14(1)	1(1)	-4(1)	-5(1)
O5	16(1)	12(1)	14(1)	2(1)	-3(1)	-4(1)
O6	12(1)	11(1)	16(1)	-1(1)	-5(1)	-2(1)
C10	13(2)	17(2)	17(2)	-2(2)	-1(2)	-4(2)
C11	36(2)	22(2)	15(2)	0(2)	-10(2)	-3(2)
C12	44(3)	24(3)	16(2)	3(2)	-11(2)	-14(2)
C13	32(2)	39(3)	23(2)	15(2)	-13(2)	-16(2)
C14	66(3)	17(3)	22(3)	5(2)	-11(2)	0(2)
C15	62(3)	18(3)	17(2)	4(2)	-15(2)	-7(2)
C20	14(2)	19(2)	11(2)	1(2)	-3(1)	-7(2)
C21	25(2)	16(2)	21(2)	1(2)	2(2)	-10(2)
C22	48(3)	22(3)	20(2)	7(2)	1 (2)	-14(2)
C23	47(3)	30(3)	18(2)	1(2)	10(2)	-18(2)
C24	34(2)	26(3)	23(2)	-2(2)	9(2)	-13(2)
C25	23(2)	18 (2)	21(2)	0(2)	0(2)	-7(2)
C30	14(2)	12(2)	14(2)	4(2)	-4(2)	-4(2)
C31	20(2)	19(2)	19(2)	-2(2)	-8(2)	-3(2)
C32	33(2)	32(3)	22(2)	-2(2)	-11(2)	-8(2)
C33	39(3)	27(3)	23(2)	-11(2)	-6(2)	-14(2)
C34	28(2)	28(3)	28(3)	-15(2)	1(2)	-5(2)
C35	19(2)	15(2)	23(2)	-5(2)	-4(2)	-2(2)
Si4	10(1)	11(1)	11(1)	1(1)	-2(1)	-3(1)
Si5	9(1)	13(1)	12(1)	1(1)	-2(1)	-3(1)
Si6	10(1)	10(1)	11(1)	0(1)	-2(1)	-2(1)
O7	14(1)	18(2)	13(1)	4(1)	-4(1)	-8(1)
O8	10(1)	12(2)	15(1)	2(1)	-4(1)	-3(1)
O9	11(1)	18(2)	15(1)	-1(1)	-3(1)	-3(1)
O10	10(1)	9(1)	18(1)	0(1)	-3(1)	-1(1)
O11	13(1)	16(2)	12(1)	-2(2)	-1(1)	-3(1)
O12	11(1)	10(1)	17(1)	0(2)	-4(1)	-3(1)
C40	16(2)	15(2)	13(2)	-2(2)	-2(2)	-5(2)
C41	18(2)	19(2)	22(2)	-3(2)	-4(2)	-7(2)
C42	20(2)	24(3)	28(2)	-11 (2)	5(2)	-4(2)
C43	31(2)	29(3)	19(2)	-10(2)	-1(2)	-5(2)

C44	34(2)	25(3)	16(2)	-2(2)	-8(2)	-14(2)
C45	16(2)	20(2)	18(2)	1(2)	-4(2)	-7(2)
C50	13(2)	15(2)	16(2)	3(2)	-3(2)	-7(2)
C51	19(2)	23(2)	15(2)	0(2)	1(2)	-7(2)
C52	33(2)	24(3)	19(2)	-8(2)	6(2)	-7(2)
C53	37(3)	32(3)	22(2)	-5(2)	13(2)	-11(2)
C54	40(3)	29(3)	20(2)	3(2)	2(2)	-14(2)
C55	32(2)	21(2)	13(2)	2(2)	1(2)	-10(2)
C60	12(2)	20(2)	11(2)	3(2)	-4(2)	-3(2)
C61	29(2)	20(2)	17(2)	-1(2)	-7(2)	-2(2)
C62	31(2)	32(3)	15(2)	2(2)	-11(2)	-6(2)
C63	36(2)	26(3)	18(2)	9(2)	-10(2)	-14(2)
C64	42(3)	20(2)	28(3)	12(2)	-15(2)	-9(2)
C65	32(2)	16(2)	21(2)	3(2)	-9(2)	-4(2)
Na1	15(1)	15(1)	18(1)	0(1)	-4(1)	-6(1)
Na2	32(1)	32(1)	28(1)	14(1)	-19(1)	-17(1)
Na3	20(1)	18(1)	21(1)	2(1)	-1(1)	-6(1)
Na4	20(1)	25(1)	21(1)	6(1)	-9(1)	-6(1)
Na5	16(1)	15(1)	21(1)	2(1)	-5(1)	-5(1)
Na6	15(1)	15(1)	22(1)	-2(1)	-4(1)	-2(1)
O13	12(1)	20(2)	16(1)	2(1)	-5(1)	-5(1)
O14	19(1)	12(2)	18(1)	-1(1)	-6(1)	-1(1)
O15	21(1)	19(2)	18(2)	0(1)	-4(1)	-6(1)
O16	23(2)	25(2)	21(2)	2(1)	-5(1)	-10(1)
O17	15(1)	20(2)	42(2)	4(2)	-4(1)	-4(1)
O18	35(2)	18(2)	33(2)	3(1)	-2(1)	-8(1)
O19	17(1)	19(2)	28(2)	5(1)	-11(1)	-4(1)
O20	15(1)	18(2)	15(1)	-1(1)	-5(1)	-5(1)
O21	22(1)	26(2)	15(1)	2(1)	-4(1)	-7(1)
O22	15(1)	26(2)	27(2)	8(1)	-7(1)	-6(1)
O23	15(1)	18(2)	15(1)	1(1)	-3(1)	-7(1)
O24	17(1)	13(2)	21(2)	0(1)	-6(1)	-3(1)
O25	16(1)	23(2)	17(1)	1(1)	-4(1)	-9(1)
O26	31(1)	17(1)	23(1)	0(1)	-4(1)	-13(1)
O27	14(1)	23(2)	31(2)	-6(1)	1(1)	-8(1)
O28	33(2)	31(2)	29(2)	9(1)	-17(1)	-13(1)
O29	16(1)	23(2)	41(2)	-12(1)	2(1)	-7(1)
O30	52(2)	28(2)	32(2)	12(1)	-16(2)	-15(2)

Table 18. Hydrogen bonds [⊕ and °]

D-H...A	D(D-H)	D(H...A)	D(D...A)	< (DHA)
O13-H13'...O11i	0.94	1.76	2.703(3)	171.5
O13-H13''...O5i	0.95	1.84	2.757(3)	163.1
O14-H14'...O11i	0.94	1.80	2.707(4)	160.3
O14- H14''...O30v	0.95	1.81	2.738(4)	166.8
O15-H15'...O10i	0.94	2.45	3.295(4)	148.5
O15-H15''...O7iv	0.95	1.87	2.775(4)	160.2
O16-H16'...O2iv	0.94	2.33	3.257(4)	165.4
O16-H16''...O5i	0.95	2.08	2.844(4)	136.6
O17-H17'...O3	0.94	1.75	2.627(4)	153.0
O17-H17''...O6i	0.95	1.82	2.760(3)	174.0
O18-H18'...O17	0.94	1.70	2.594(4)	156.2
O18-H18''...O19	0.95	2.46	3.244(4)	140.5
O19-H19'...O5	0.94	1.76	2.684(4)	164.3
O19-H19''...O27	0.95	2.19	2.941(4)	135.6
O20-H20'...O9i	0.94	1.73	2.672(3)	171.1

O20-H20''...O13	0.95	1.82	2.766(3)	177.2
O21-H21'...O29	0.94	2.03	2.970(4)	171.9
O21-H21''...O5	0.95	1.88	2.785(3)	160.4
O22-H22'...O12	0.94	2.08	2.809(3)	133.2
O23-H23'...O1iv	0.94	1.79	2.728(3)	175.4
O23-H23''...O7iv	0.95	1.85	2.730(3)	154.2
O24-H24'...O1iv	0.94	1.75	2.665(4)	162.3
O24-H24''...O18	0.95	1.88	2.787(4)	161.3
O25-H25'...O23vi	0.94	2.00	2.898(3)	157.0
O25-H25''...O3iii	0.95	1.75	2.659(4)	161.4
O26-H26'...O1	0.94	1.84	2.761(3)	164.3
O26-H26''...O13iii	0.95	2.26	2.986(4)	133.3
O26-H26''...O17iii	0.95	2.33	3.013(4)	128.4
O27-H27'...O3vii	0.94	1.87	2.819(4)	177.5
O27-H27''...O1iv	0.95	1.92	2.849(3)	166.9
O28-H28''...O7iv	0.95	1.75	2.628(4)	153.6
O29-H29'...O9i	0.94	1.95	2.797(4)	148.3
O29-H29''...O11	0.95	1.81	2.755(3)	174.1
O30-H30'...O22iii	0.95	1.75	2.687(4)	169.5

Symmetry Transformations used to generate equivalent atoms:

(i) x+1,y,z (ii) x-1,y,z (iii) x+1,y-1,z (v) x+2,y-1,z (vi) x-2,y+1,z (vii) x,y-1,z

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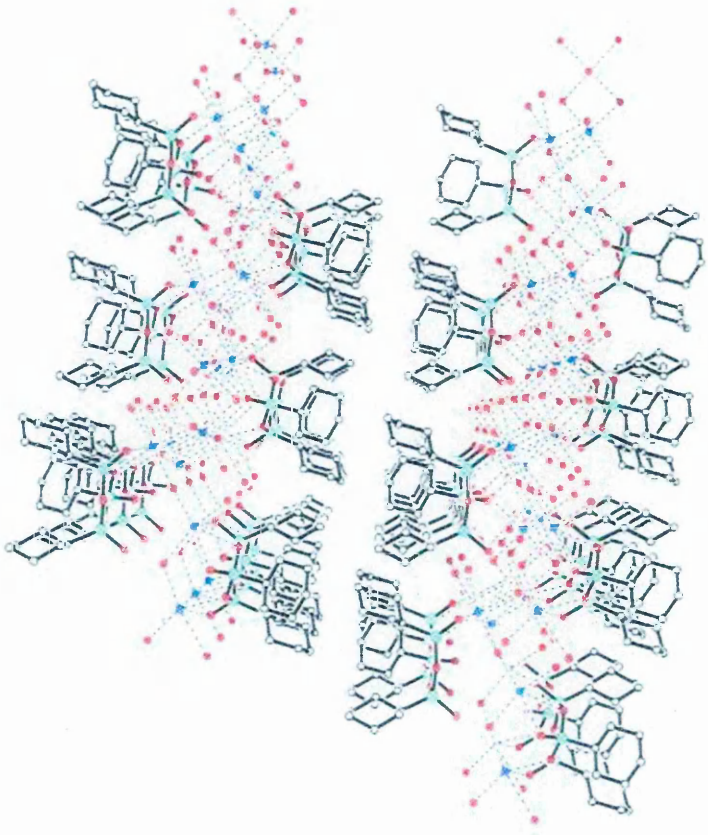

Figure 4 - cyclohexyl sodium siloxysilanolate.

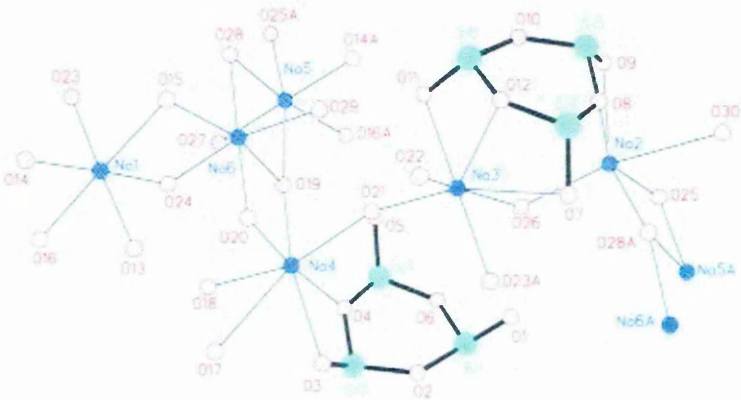

Figure 5 - cyclohexyl sodium siloxysilanolate lateral view.

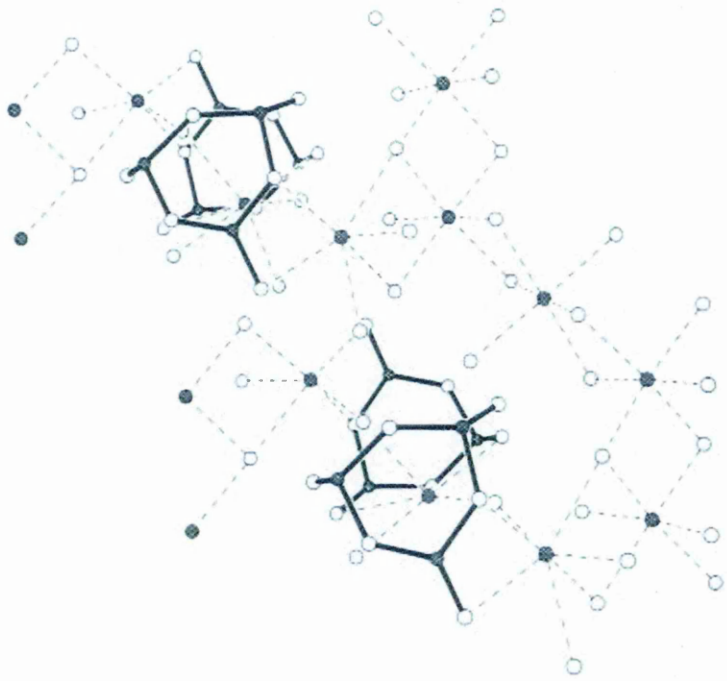

Figure 6 - cyclohexyl sodium siloxysilanolate front view.

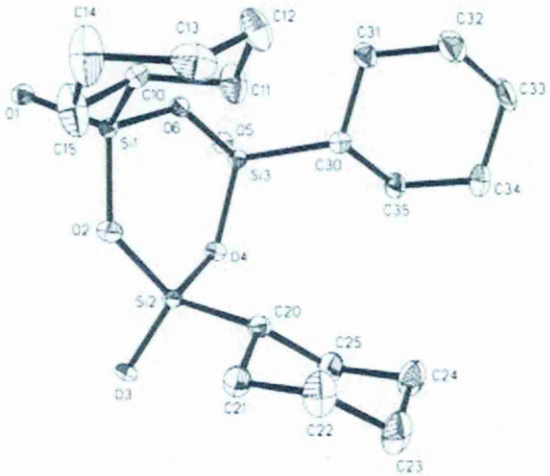

Figure 7 a.

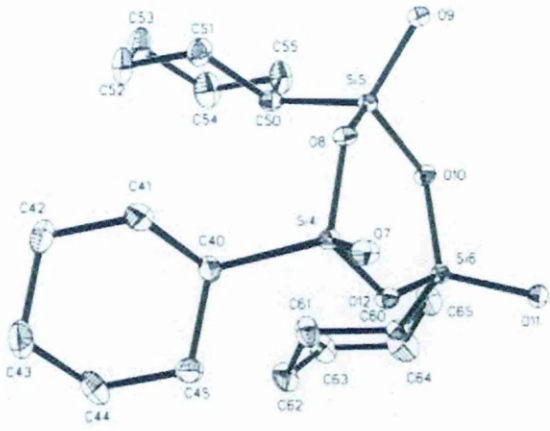
C53
C51
C55
O9
C52
C54
C50
Si5
O8
O10
C41
C42
Si4
O7
C40
Si6
O12
C61
C60
C65
O11
C43
C63
C64
C45
C62
C44

Figure 7 b.